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AND
WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.

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[SIXTH SERIES.]

JULY 1912.

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I. *On the Magnetic Properties of a Graded Series of Nickel-Manganese Alloys.* By JAMES G. GRAY, *D.Sc., Lecturer on Physics in the University of Glasgow*[*].

[Plate I.]

THE magnetic properties of iron, steel, nickel, and cobalt at moderate and high temperatures have been investigated by numerous experimenters, notably by Rowland[†], Baur[‡], Trowbridge[§], Perkins[‖], Tomlinson[¶], and Hopkinson[**]. For the above mentioned metals it was shown (for temperatures lying between room-temperature and the so-called critical temperatures of the materials) that the effect of a rise in temperature is to bring about an increase in the susceptibility for low values of the magnetizing force, and a diminution for large values. Thus if we denote the magnetization curves corresponding to temperatures t_1 and t_2 ($t_2 > t_1$) by A and B respectively, the curve A lies at first below, and finally above, the curve B, provided that the magnetizing force is pushed far enough.

To account for this result Hopkinson regarded the iron or steel as made up of permanently magnetic molecules, the axes of which become more or less directed to parallelism by magnetic force. The effect of rise in temperature is to diminish the magnetic moment of the molecules, gradually at first, but more and more rapidly as the critical temperature is approached. On the other hand, the freedom with which the molecules have their axes directed increases with rise of temperature. For low values of the magnetizing force the increased freedom of the molecules brought about by increase in the temperature more than compensates for the diminution in the magnetic moment of the molecular magnets, with the result that the susceptibility of the test-piece is increased. For high values of the magnetizing force the reverse is the case.

---

[*] Communicated by Professor Andrew Gray, F.R.S.

[†] Phil. Mag. xlviii. p. 321 (1874).

[‡] Wied. *Ann.* xi. p. 394 (1880).

[§] Proc. Amer. Acad. p. 462 (1885).

[‖] Sill. Journ. xxx. p. 218 (1885).

[¶] Phil. Mag. xxv. p. 372 (1888).

[**] Proc. Roy. Soc. xlv. p. 318 (1889).

From this point of view we should expect to find that the effect of immersing a test-specimen of iron or steel in liquid air, and thus bringing it to a temperature of −190° C., would be to diminish its susceptibility for low fields and increase it for high fields. That this is the case for annealed iron, nickel, and cobalt, has been proved by Honda and Shimizu [*], who examined specimens of these metals (1) at room-temperature, and (2) when immersed in liquid air. The improvement in magnetic quality brought about by the low temperature for high fields is very slight, and the value of the magnetizing force for which the magnetization curves cross is very great, in the case of these materials.

In 1890 Hopkinson [†] described the very remarkable magnetic properties of the material resulting from alloying iron with nickel. Although both these metals belong to the magnetic group, an alloy of the two, containing 25 per cent. nickel, is quite non-magnetic at ordinary room-temperature when in the forged or annealed conditions. If cooled to a temperature considerably below 0° C., however, it becomes magnetic, and remains magnetic on warming to room-temperature. The critical temperature of a specimen after being cooled was found by Hopkinson to be about 600° C.; that is, the specimen retained a considerable amount of magnetic susceptibility for temperatures lying between room-temperature and 600° C. On being heated to this latter temperature the test-piece became non-magnetic, and remained so on cooling to that of the room. On cooling the specimen once more the magnetic condition was restored.

Specimens of nickel-steel containing varying amounts of nickel and iron were examined by Hopkinson, and yielded results of great interest. In general the specimens were found to possess a considerable amount of magnetic quality at room-temperature in the annealed condition. The alloy containing 25 per cent. nickel was the only member of the series which was non-magnetic at room-temperature in the annealed condition.

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[*] Phil. Mag. x. p. 548 (1905).

[†] Proc. Roy. Soc., Dec. 12, 1889; May 1, 1890.

The low temperatures employed by Hopkinson in his experiments were obtained by means of carbonic-acid snow. It has since been found that if a nickel-steel specimen is tested in the annealed condition at room-temperature, and again at the temperature of liquid air, a considerable improvement in its magnetic quality is brought about by the cooling. If the specimen is allowed to warm to room-temperature a further improvement takes place in the magnetic quality. Thus, so far as its magnetic properties are concerned, the material has been transformed in the process of cooling. Reannealing from 900° C. results in the specimen being restored to its original condition of inferior magnetic quality.

Nickel-steel is not the only iron alloy which exhibits this remarkable absence of magnetic quality. The material known as Hadfield's "manganese-steel," which is iron alloyed with 12 per cent. manganese, is practically non-magnetic under ordinary conditions. Its permeability is about 1·4, and is practically constant in strong and weak magnetic fields. A specimen of this material exhibits no residual magnetism, even after having been exposed to a very powerful magnetizing force.

Heusler* in 1903 made the interesting discovery that alloys of copper, manganese, and aluminium are strongly magnetic. By properly adjusting the amounts of the component metals present an alloy is obtained, the magnetic susceptibility of which is comparable with that of cast iron. In Hopkinson's nickel-steel containing 25 per cent. nickel we have an example of an alloy composed of two magnetic metals, which is itself non-magnetic at room-temperature in the annealed condition. Heusler's alloy, on the other hand, which is strongly magnetic, is composed entirely of non-magnetic metals.

The important part played by nickel in Hopkinson's nickel-steels, and by manganese in the Heusler alloys and in Hadfield's manganese-steels, led the writer to believe that it would be of interest to investigate the magnetic properties of a series of alloys composed of nickel and manganese in varying proportions. A set of specimens was accordingly cast in the form of cylindrical rods, each about 21 cm. long, and having a diameter of 0·9 cm. The series was built up as follows: 5 per cent. Mn, 95 per cent. Ni; 10 per cent. Mn, 90 per cent. Ni; and so on up to 30 per cent. Mn, 70 per cent. Ni. On account of the fact that hot manganese absorbs carbon with great readiness, special precautions had to be taken to prevent admission of this element. The alloying was conducted in a "Salamander" crucible under a layer of fused barium chloride; charcoal cannot be used if the percentage of manganese present is appreciable. The metal was cast in dry sand moulds lined with whiting.

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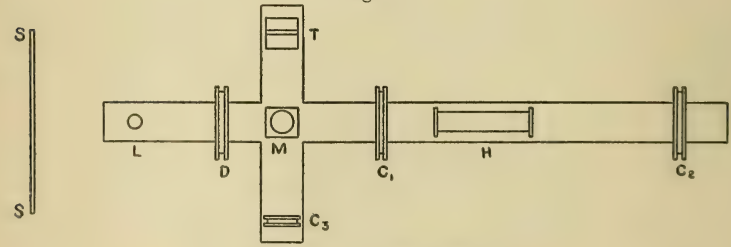
* *Verh. d. deutsch. Phys. Ges.* v. p. 219 (1903).

The specimens were tested at room-temperature and at —190° C. (when immersed in boiling liquid air) in each of the following conditions: (1) as cast, (2) after annealing at 900° C., (3) after quenching at 900° C. Condition (2) of the metal was attained by imbedding the specimen in kaolin clay contained within an iron tube, and enclosing the whole in a Fletcher gas furnace. In this way the specimen could be brought to 900° C., and cooled very gradually whilst out of contact with the atmosphere. After testing the specimen in the annealed condition it was brought to a temperature of 900° C. and plunged vertically into ice-cold water; it was then in condition (3).

The magnetic tests were made by means of a magnetometer specially designed by Dr. A. D. Ross* and the writer for the carrying out of investigations of this kind. The main features of the instrument (fig. 1) are the simple and novel methods introduced for rapidly securing accurate compensation for the effect at the needle produced by the field of the magnetizing solenoid. The magnetometer proper M, the solenoid H, the compensating coils C_1, C_2, C_3, and the lamp L for showing the movement of the magnetometer needle, are all mounted on a strong mahogany base-board, and move freely in channelled beds. They can be firmly fixed by means of friction clamps; C_1 is the principal compensating coil, C_2 a coil for fine adjustment, while C_3 removes any error due to want of proper alignment of C_1, C_2, and the solenoid. The method of adjusting the apparatus for use is as follows.

Fig. 1.



Plan of the magnetometer.

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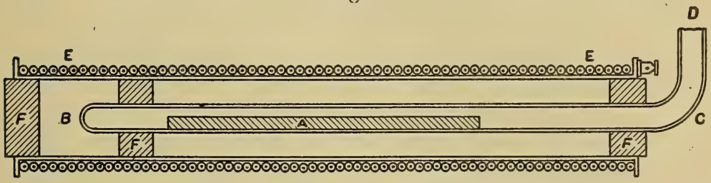
* Phil. Mag. July 1909.

The solenoid is first clamped in a convenient position, and a current considerably greater than the greatest current to be employed in the tests is sent through the coils C_1, C_2, and the solenoid. Compensation, for the central position of the spot on the scale, is then obtained roughly by moving the coil C_1 away from or towards the solenoid: the coil C_1 is then clamped. The coil C_2 is now moved in or out until the spot is brought back exactly to the zero of the scale, and is then clamped in position. The effect of the field at the needle due to the solenoid is now eliminated, so far as the equilibrium position of the needle is concerned. If, however, as is inevitable, the centres of the coils C_1 and C_2, the needle and the axis of the solenoid are not in one line, the balance will not hold for the deflected position of the needle. The coil C_3, the axis of which lies on the north and south line passing through the needle, is now included in the circuit, and, by means of a small magnet carried on a stand, the spot is brought to one extreme position of the scale. The coil C_3 is then moved towards or away from the needle until no movement of the spot follows upon the reversal of a large current in the circuit. This operation having been completed, the magnetometer is in complete adjustment.

In the magnetic tests the specimen was mounted within the magnetizing solenoid in the manner shown in fig. 2.

Fig. 2.



Method of cooling the specimens to −190° C.

A is the specimen contained within a glass tube (BCD), one end of which was closed, while the other end, CD, was open and curved upwards. The tube was supported by cork bungs, FF, so that the specimen lay along the axis of the solenoid. Previous to being tested the specimen was subjected to the action of an alternating magnetic field, which gradually diminished from a large value to zero, that is to a "process of reversals." It was then tested at room-temperature. Liquid air was now poured into the tube, and the specimen cooled to −190° C. In all the experiments now described the specimen was kept immersed in liquid air for

30 minutes before measurements were made. The specimen was now subjected to a "process of reversals" and tested. Finally, with a view to ascertaining whether the cooling to −190° C. had transformed the material, the specimen was allowed to warm to room-temperature, and then again subjected to the action of a "process of reversals" and tested. This procedure was gone through for each specimen in each of the three conditions specified above.

It is well known that before a magnetic test is commenced all traces of previous magnetic operations must be eliminated from the specimen. This is accomplished by subjecting the specimen to the action of a "process of reversals." But it is far from well known that any thermal treatment applied to a specimen between its neutralization by the "process of reversals" and the magnetic tests which follow is fatal to accurate work. A specimen rendered neutral at one temperature ceases to be neutral if the temperature is changed. Before carrying out tests at a definite temperature following upon temperature change it is essential that the specimen should be subjected to a "process of reversals" at the new temperature. This important fact has been clearly shown by a number of experiments carried out by Dr. A. D. Ross[*] and the writer.

In Pl. I. fig. 3 are shown the magnetization curves yielded by a specimen of pure nickel when tested, at room-temperature and at −190° C., in the annealed and quenched conditions. It will be seen that for both conditions of the metal the magnetization curve corresponding to the liquid-air temperature lies everywhere below that corresponding to room-temperature. The curves show that had the magnetizing force been pushed to a sufficiently high value crossing of the curves for the two temperatures would have taken place; but for pure annealed or quenched nickel the susceptibility at −190° C. is less than that at room-temperature for all fields lying between 0 and 200 C.G.S. units.

The results obtained on testing the nickel-manganese specimen containing 5 per cent. Mn are shown in Table I. and in Pl. I. fig. 4. The addition of the manganese has brought about very marked changes in the magnetic properties of the material. The susceptibility of the alloy in the annealed condition is inferior to that of pure annealed nickel for all values of the magnetizing force. For this condition of the alloy crossing of the magnetization curves corresponding to 15° C. and −190° C. occurs for a value of the magnetizing force of 45 C.G.S. units. For H = 200 C.G.S.

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[*] See Phil. Mag. [6] xxi. p. 1 (1911).

units the values of the intensity of magnetization are 316 and 350 C.G.S. units at 15° C. and −190° C. respectively.

TABLE I.—Nickel-Manganese Specimen ; 5 per cent. Mn.

Value of H.	Specimen as cast.				Specimen after annealing from 900° C.				Specimen after quenching at 900° C.			
	$t=16°$ C.		$t=-190°$ C.		$t=16°$ C.		$t=-190°$ C.		$t=16°$ C.		$t=-190°$ C.	
	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.
5 ...	18	3·60	15	3·00	20	4·00	16	3·20	38	7·60	30	6·00
10 ...	44	4·40	38	3·80	48	4·80	40	4·00	67	6·70	60	6·00
15 ...	68	4·53	64	4·26	77	5·13	66	4·40	92	6·13	89	5·92
20 ...	86	4·30	83	4·15	97	4·85	89	4·45	110	5·50	110	5·50
40 ...	139	3·48	143	3·57	158	3·95	155	3·87	162	4·05	172	4·30
60 ...	177	2·95	187	3·11	195	3·25	203	3·38	196	3·26	212	3·53
80 ...	209	2·61	220	2·75	224	2·80	236	2·95	225	2·81	244	3·05
100 ...	232	2·32	244	2·44	248	2·48	264	2·64	249	2·49	271	2·71
150 ...	272	1·81	290	1·93	292	1·95	317	2·11	293	1·95	320	2·13
200 ...	291	1·45	312	1·56	316	1·58	350	1·75	318	1·59	353	1·76

The behaviour of the specimen after quenching exhibits some remarkable features. In the first place the susceptibility for low fields is found to have undergone a marked improvement. At room-temperature the intensity of magnetization is found to be 38 C.G.S. units for a field of 5 C.G.S. units, as against 20 C.G.S. units for the material in the annealed condition. Crossing of the I–H curves at 15° C. and −190° C. takes place for a value of the magnetizing force of 20 C.G.S. units. For field-strengths greater than this value the susceptibility of the material is practically that which is characteristic of the annealed specimen.

The results obtained on testing a specimen containing 10 per cent. Mn are exhibited in Table II. and in Pl. I. fig. 5. The specimen exhibited properties whose general features are similar to those shown by the specimen previously described. The improvement in magnetic quality for high fields brought about by cooling to the temperature of liquid air is, however, much greater. For the annealed condition of the alloy the I–H curves corresponding to 15° C. and −190° C. cross for a value of the magnetizing force of 24 C.G.S. units; for the quenched alloy they cross for H = 10 C.G.S. units. The improvement in magnetic quality which follows upon the cooling is very great for high fields. For the annealed material at 15° C. the intensity of magnetization is 368 C.G.S. units for H = 200 C.G.S. units as against

434 c.g.s. units for the cooled specimen when exposed to the same magnetizing force.

Table II.—Nickel-Manganese Specimen; 10 per cent. Mn.

Value of H.	Specimen as cast.				Specimen after annealing from 900° C.				Specimen after quenching at 900° C.			
	$t=16°$ C.		$t=-190°$ C.		$t=16°$ C.		$t=-190°$ C.		$t=16°$ C.		$t=-190°$ C.	
	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.
5 ...	30	6·00	22	4·40	30	6·00	26	5·20	46	9·20	37	7·40
10 ...	74	7·40	60	6·00	75	7·50	60	6·00	86	8·60	86	8·60
15 ...	104	6·93	94	6·26	109	7·26	97	6·46	116	7·72	126	8·40
20 ...	125	6·25	120	6·00	130	6·50	129	6·45	140	7·00	152	7·60
40 ...	190	4·75	206	5·15	212	5·30	224	5·60	204	5·10	226	5·65
60 ...	236	3·93	264	4·40	258	4·30	280	4·66	240	4·00	276	4·90
80 ...	267	3·34	306	3·83	287	3·59	318	3·98	270	3·38	316	3·95
100 ...	288	2·88	336	3·36	308	3·08	353	3·53	288	2·88	345	3·45
150 ...	321	2·14	384	2·56	344	2·30	404	2·70	322	2·14	398	2·66
200 ...	336	1·68	416	2·08	368	1·84	434	2·17	344	3·44	428	2·14

As in the case of the specimen containing 5 per cent. Mn, quenching the specimen had the effect of considerably improving its magnetic susceptibility for low field-strengths. For H = 10 c.g.s. units the susceptibility of the quenched specimen at room-temperature was 8·6 as against the value 7·5 for the annealed specimen at the same temperature. For fields greater than about 30 c.g.s. units, however, the susceptibility of the quenched specimen at room-temperature was less than that of the annealed specimen.

The results yielded by the specimen containing 15 per cent. Mn are shown in Table III., and the magnetization curves in Pl. I. fig. 6. The susceptibility of this material in the cast and annealed conditions for low and moderate field-strengths is greater than that of the alloy containing 10 per cent. Mn. Thus for the annealed conditions of the two alloys the susceptibilities of the 10 per cent. and 15 per cent. Mn specimens at room-temperature, and for a field-strength of 10 c.g.s. units, were found to be 7·5 and 11·5 respectively; for H = 20 c.g.s. units the corresponding values were 6·5 and 8·4. For high field-strengths, however, the susceptibility of the annealed specimen containing 15 per cent. Mn was decidedly lower than that of the 10 per cent. Mn specimen in the same condition.

Table III.—Nickel-Manganese Specimen ; 15 per cent. Mn.

Value of H.	Specimen as cast.				Specimen after annealing from 900° C.				Specimen after quenching at 900° C.			
	$t=16°$ C.		$t=-190°$ C.		$t=16°$ C.		$t=-190°$ C.		$t=16°$C.		$t=-190°$ C.	
	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.
5 ...	46	9·20	30	6·00	68	13·60	42	8·40	22	4·40	20	4·00
10 ...	80	8·00	70	7·00	115	11·50	100	10·00	48	4·80	62	6·20
15 ...	104	6·92	112	7·46	148	9·86	146	9·72	63	4·20	88	5·86
20 ...	123	6·15	142	7·10	167	8·35	176	8·80	75	3·75	108	5·40
40 ...	166	4·15	232	5·80	214	5·35	262	6·55	108	2·70	178	4·45
60 ...	190	3·17	276	4·90	240	4·00	316	5·27	126	2·10	226	3·75
80 ...	204	2·55	306	3·82	256	3·20	344	4·30	140	1·75	262	3·28
100 ...	214	2·14	330	3·30	268	2·68	368	3·68	151	1·51	288	2·88
150 ...	228	1·52	368	2·46	288	1·92	410	2·74	169	1·12	334	2·22
200 ...	236	1·18	392	1·96	304	1·52	438	2·19	180	0·90	366	1·83

For this alloy in all three conditions the effect of cooling the specimen to the temperature of liquid air was to bring about a very decided improvement in its magnetic qualities for high values of the magnetizing force and a diminution for low values. In the annealed condition of the specimen the magnetization curves corresponding to room-temperature and −190° C. crossed for a value of H of 14 c.g.s. units ; in the quenched condition of the material the curves crossed for a value of H of 7 c.g.s. units.

The effect of quenching the specimen was to largely destroy its magnetic quality. In this condition its susceptibility at −190° C. is vastly greater than at room-temperature. For H=200 c.g.s. units the values of the intensity of magnetization at room-temperature and −190° C. are 180 and 366 c.g.s. units respectively.

The specimen having the composition 20 per cent. Mn, 80 per cent. Ni gave the results shown in Pl. I. fig. 7 and in Table IV. Both in the cast and the annealed conditions this specimen was found to be, comparatively speaking, slightly magnetic. The effect of cooling it to −190° C. was to bring about a very great improvement in magnetic quality. In the annealed condition of the material the intensity of magnetization for a field-strength of 20 c.g.s. units is 47 c.g.s. units at room-temperature; at −190° C. it is 123 c.g.s. units; for a field of 200 c.g.s. units the values of the intensity of magnetization at the two temperatures are 110 and 296 c.g.s. units respectively.

TABLE IV.—Nickel-Manganese Specimen : 20 per cent. Mn.

Value of H.	Specimen as cast.				Specimen after annealing from 900° C.				Specimen after quenching at 900° C.			
	t=16°C.		*t*=−190° C.		*t*=16° C.		*t*=−190° C.		*t*=16° C.		*t*=−190° C.	
	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.
5 ...	16	3·20	7	1·40	20	4·00	30	6·00	1·0	0·25	27	5·40
10 ...	26	2·60	26	2·60	32	3·20	70	7·00	1·5	0·15	51	5·10
15 ...	34	2·27	52	3·46	41	2·73	99	6·60	2·0	0·12	64	4·26
20 ...	40	2·00	80	4·00	47	2·35	123	6·15	2·5	0·12	78	3·90
40 ...	56	1·40	148	3·70	64	1·60	181	4·52	3·5	0·08	112	2·80
60 ...	65	1·08	179	2·98	76	1·27	216	3·60	4·5	0·07	131	2·18
80 ...	72	0·9	202	2·52	85	1·06	236	2·95	5·0	0·06	146	1·83
100 ...	77	0·77	218	2·18	91	0·91	250	2·50	5·5	0·05	158	1·58
150 ...	90	0·60	248	1·66	102	0·68	276	1·84	6·0	0·04	177	1·18
200 ...	96	0·48	270	1·35	110	0·55	296	1·48	6·5	0·03	192	0·96

In the experiments now described the lowest field employed was 5 C.G.S. units. For this alloy in the annealed condition this field-strength produced an intensity of magnetization of 20 C.G.S. units and 30 C.G.S. units at 15° C. and −190° C. respectively. Thus the magnetization curves corresponding to the two temperatures cross, if they do cross, for a very low value of the magnetizing force.

The effect of quenching this material is in large measure to destroy its magnetic quality. At room-temperature the quenched specimen was practically non-magnetic, the intensity of magnetization for a field-strength of 200 C.G.S. units being only 6 C.G.S. units. At the temperature of liquid air, however, the specimen exhibited very considerable magnetic quality. For H = 20 C.G.S. units the intensity of magnetization of the quenched material at −190° C. was 78 C.G.S. units as against 2·5 C.G.S. units for room-temperature ; for H = 200 C.G.S. units the intensity of magnetization at −190° C. was 192.

It may be mentioned at this stage that in the case of all these nickel-manganese alloys, in all the three conditions, no transformation of the material is brought about by cooling to the liquid-air temperature ; the magnetization curve at room-temperature following upon cooling to −190° C. is practically identical with that obtained at room-temperature before cooling. Thus in the case of the specimen containing 20 per cent. Mn the effect of quenching at 900° C. has been to lower the critical temperature to the neighbourhood of room-temperature. This particular specimen was set aside in the quenched condition for five months and then retested, when it was found that no alteration had taken place in its magnetic properties. Reannealing at 900° C. resulted in its being restored to the condition which is characteristic of the material in the freshly annealed condition.

In Tables V. and VI. and Pl. I. figs. 5 and 6, are shown the results obtained on testing specimens containing 25 per cent. Mn and 30 per cent. Mn respectively. These materials are, comparatively speaking, weakly magnetic. The magnetization curves for these specimens are very similar in

Table V.—Nickel-Manganese Specimen; 25 per cent. Mn.

Value of H.	Specimen as cast.				Specimen after annealing from 900° C.				Specimen after quenching at 900° C.			
	t=16° C.		*t*=−190° C.		*t*=16° C.		*t*=−190° C.		*t*=16° C.		*t*=−190° C.	
	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.
5 ...	4	0·80	6	1·20	6	1·20	10	2·00	3	0·60	4	0·80
10 ...	9	0·90	16	1·60	12	1·20	24	2·40	6	0·60	8	0·80
15 ...	15	1·00	27	1·80	18	1·20	38	2·52	10	0·66	12·5	0·83
20 ...	21	1·05	39	1·95	28	1·40	51	2·55	13	0·65	16	0·80
40 ...	45	1·12	76	1·90	58	1·45	94	2·35	29	0·72	33	0·83
60 ...	61	1·01	106	1·77	80	1·33	130	2·16	40	0·66	48	0·80
80 ...	74	0·93	130	1·62	96	1·20	156	1·95	50	0·62	60	0·75
100 ...	85	0·85	149	1·49	109	1·09	180	1·80	56	0·56	72	0·72
150 ...	107	0·71	186	1·24	131	0·88	217	1·45	70	0·46	94	0·63
200 ...	120	0·60	214	1·07	147	0·73	247	1·23	81	0·40	114	0·57

Table VI.—Nickel-Manganese Specimen; 30 per cent. Mn.

Value of H.	Specimen as cast.				Specimen after annealing from 900° C.				Specimen after quenching at 900° C.			
	t=16° C.		*t*=−190° C.		*t*=16° C.		*t*=−190° C.		*t*=16° C.		*t*=−190° C.	
	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.	I.	K.
5 ...	2	0·40	3	0·60	2	0·40	3	0·60	1	0·20	1	0·20
10 ...	4	0·40	6	0·60	4	0·40	6	0·60	3	0·30	3	0·30
15 ...	7	0·46	10	0·66	7	0·47	10	0·66	4	0·27	4	0·27
20 ...	9	0·45	13	0·65	11	0·55	14	0·70	6	0·30	7	0·35
40 ...	28	0·70	32	0·80	30	0·75	35	0·87	16	0·40	17	0·43
60 ...	46	0·77	51	0·85	48	0·80	54	0·90	27	0·45	29	0·48
80 ...	61	0·77	67	0·84	67	0·84	72	0·90	36	0·45	39	0·49
100 ...	74	0·74	81	0·81	81	0·81	89	0·89	43	0·43	46	0·46
150 ...	102	0·68	111	0·75	112	0·75	123	0·82	57	0·38	61	0·41
200 ...	121	0·62	134	0·67	135	0·67	152	0·76	68	0·34	72	0·36

general features to those which were furnished by the specimens containing lower percentages of manganese. For all the field-strengths employed the susceptibility is greater at −190° C. than at room-temperature.

The effect of quenching was in both cases to diminish greatly the susceptibility for all fields, and in these specimens the improvement brought about in the magnetic quality of the quenched material by cooling to −190° C. was comparatively slight.

Complete hysteresis curves for the specimens containing 15 per cent. and 20 per cent. manganese in the annealed and quenched conditions are shown in Pl. I. figs. 10 and 11. It will be seen that in these alloys the hysteresis is much greater at −190° C. than at room-temperature. The curves show that the coercive force is small for both materials.

It is interesting to contrast the behaviour of these manganese-nickel alloys with that exhibited by the manganese- and nickel-steels. The effect of alloying iron with manganese is to mask to a great extent the magnetic properties of the iron. Specimens of manganese-steel containing less than 12 per cent. of manganese are magnetic, but much less so than would be expected from the amount of iron present. Manganese-steel containing 9 per cent. of manganese is slightly magnetic, and if the percentage of manganese is greater than 12 the resulting material is practically non-magnetic. The magnetic manganese-steels are transformed in magnetic quality by cooling to the temperature of liquid air. If a specimen containing 6 per cent. of manganese, for example, is examined in the annealed condition (1) at room-temperature, (2) at −190° C., and (3) at room-temperature following upon cooling to −190° C., and the magnetization curves yielded by the three sets of tests plotted, it will be found that the curve corresponding to (3) will lie everywhere above that corresponding to (2), and that the curve corresponding to (2) lies everywhere above that corresponding to (1).

The behaviour of the nickel-steels is very similar to that of the manganese-steels. The magnetic quality of iron is greatly reduced by the addition of nickel, and the alloys are transformed by cooling to the temperature of liquid air.

The effect of alloying nickel with manganese is to diminish the susceptibility of the nickel, but the alloys are distinctly magnetic, even when the percentage of manganese is 30. These alloys are not transformed by cooling to −190° C.

It has already been pointed out that on Hopkinson's theory we should expect to find the susceptibility of a magnetic material diminished for low fields and increased for high fields by cooling to the temperature of liquid air, provided that the material is not transformed. This is characteristic of iron, nickel, cobalt, and the carbon steels. It is shown in a very marked degree by these nickel-manganese alloys. The magnetization curves corresponding to room-temperature and −190° C. cross for values of the magnetizing force which are small compared with those required to bring about crossing of the curves for iron, nickel, and cobalt, and the increase in susceptibility brought about by the cooling is enormously greater than is the case for these metals.

Summary.

1. Specimens of pure nickel and of nickel-manganese alloys containing 5 per cent., 10 per cent., ..., 30 per cent. Mn respectively were tested at room-temperature and at −190° C. (when immersed in boiling liquid air) in the conditions brought about by

(1) the process of casting;
(2) annealing at 900° C.;
(3) quenching at 900° C.

2. In pure nickel the effect of cooling to −190° C. is to diminish the susceptibility for low fields and to increase it for high fields; the value of H for which the magnetization curves corresponding to 15° C. and −190° C., respectively, cross is greater than 200 C.G.S. units.

3. The effect of adding manganese to nickel is to diminish the susceptibility of the nickel. The resulting material behaves normally, in that a magnetization curve corresponding to −190° C. lies initially below and finally above that corresponding to 15° C. This is characteristic of the material in all three conditions.

4. For the nickel-manganese alloy containing 5 per cent. Mn in the annealed condition magnetization curves for 15° C. and −190° C. cross for H=45 C.G.S. units. For H=200 C.G.S. units the values of the intensity of magnetization at the two temperatures are 316 and 350 C.G.S. units respectively. Quenching this material enhanced its susceptibility for low fields. For this condition of the metal crossing of the I–H curves took place for a value of the magnetizing force of 20 C.G.S. units.

5. The behaviour of the alloy of nickel with manganese containing 10 per cent. Mn was very similar to that exhibited

by the specimen containing 5 per cent. Mn. The improvement in magnetic quality for high fields is, however, much greater in this material. In the annealed condition of the metal the magnetization curves corresponding to 15° C. and −190° C. cross for H = 24 C.G.S. units, the curves for the quenched material at the two temperatures cross for H = 10 C.G.S. units. Quenching this material at 900° C. improves its magnetic quality for low fields.

6. The material resulting from alloying nickel with 15 per cent. Mn behaves normally in that the magnetization curve corresponding to −190° C. lies at first below and finally above that corresponding to 15° C. The curves cross for H = 14 C.G.S. units for the annealed material, and for H = 7 C.G.S. units for the quenched material. The improvement in magnetic quality for high fields produced by cooling a specimen is very great.

7. The nickel-manganese alloy containing 20 per cent. manganese exhibited very remarkable magnetic properties. In all conditions of the metal the magnetization curves yielded on testing the specimen at 15° C. and −190° C. cross for very small values of the magnetizing force, and the improvement in magnetic quality brought about by cooling to the temperature of liquid air is enormous. Quenching a specimen at 900° C. rendered it non-magnetic at room-temperature. At −190° C., however, it exhibited very decided magnetic properties.

8. Specimens containing 25 and 30 per cent. of manganese were tested in all three conditions at 15° C. and −190° C. They were found to be feebly magnetic. The magnetization curves at the two temperatures cross for very small values of the magnetizing force.

9. Unlike the manganese- and nickel-steels, the nickel-manganese alloys are not changed in magnetic quality by being cooled to the temperature of liquid air. A magnetization curve yielded by a specimen at room-temperature, following upon cooling to −190° C., is practically identical with that yielded by the specimen at room-temperature previous to being cooled.

The work described in this paper was carried out in the Natural Philosophy Institute of the University of Glasgow, and the author desires to express his thanks to Professor Gray for the interest he has taken in the progress of the experiments.

II. *Some Experiments on the Electrical Behaviour of Metallic Vapours in Flames.* *By* E. N. da C. Andrade, *Ph.D.*, *B.Sc.*, 1851 *Exhibition Scholar of University College, London* *.

§ 1. *Introduction.*

THE following work, carried out in the Radiologisches Institut of Heidelberg, falls into two parts, the first part (§ 2–§ 5) being concerned with some of the properties—deviation in the electric field †, conductivity, light-emission—of metallic vapour in the Bunsen flame; the second part (§ 6–§ 11) deals with the variation of the deviation of the streak of vapour with pressure, both when this is above and below atmospheric, and was undertaken with the particular object of throwing light on the mechanism of the liberation of the electron from the metallic atom in the flame.

The first experiments to be described show that in certain circumstances there exist negatively-charged luminous metal atoms in the flame. The conductivity of the vapour has been measured under new conditions, and hence an estimate of the number of free electrons produced per second in the vapour made. A proportionality between luminosity and conductivity has been found.

In the second part, the chief result has been to show that the velocity of migration of the positive metallic carriers is inversely proportional to the pressure, which leads to the conclusion that the fraction of time during which a metal atom in the luminous streak is positively charged (we make the assumption ‡ that the atom is alternately positive and neutral) is independent of the pressure. As a theoretical result of this we have that the impact of metal atom against metal, as distinct from that of metal atom against gas molecule, is mainly responsible for the liberation of the electron.

Measurements on the variation of conductivity and light emission with pressure are also described.

§ 2. *General behaviour of the Luminous Streak in the Electric Field.*

As it was desired to measure the deflexion of the luminous streak of metallic vapour in the flame with a range of pressures, it was advisable to study the phenomena generally at atmospheric pressure. G. Ebert[*] has observed that the amount of deflexion of the streak in an electric field depends markedly upon the amount of salt vaporized: he records that with diminishing amounts of salt vaporized in a given time the deviation of the streak, after at first diminishing rapidly, finally becomes constant for amounts of salt less than a given value. As this constant value was of particular interest, Ebert confined himself to examining the effect with small amounts of salt.

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* Communicated by Prof. Sir J. J. Thomson.

† The deviation in an electric field of the streak of metallic vapour formed when a bead of metallic salt is brought into the flame which was observed by P. Lenard, *Ann. der Physik* (4) ix. p. 642 (1902).

‡ Made by Lenard for the positive carriers in flames (*loc. cit.*), and subsequently by W. Wien for canal rays.

It seemed to me of interest to study the phenomena with very strong streaks, *i. e.*, with a large amount of salt present, and consequent rapid vaporization. Under these circumstances a new phenomenon appears: part of the streak is deflected towards the positive electrode, and thus must be negatively charged. The negatively charged part of the coloured streak is always smaller than the positive part, but there is no doubt as to its existence. It exists throughout the flame, and not in any particular zone: to investigate this one of the electrodes was replaced by a net, which facilitates observation.

The question arises, when does this phenomenon of a negative deflexion begin to make its appearance? It seems to take place to some extent even for a faint streak, *i. e.*, the side of the streak towards the positive electrode is less deflected than the other side of the streak towards the negative electrode. The deflexion of the flame as a whole towards the negative electrode tends to hide this; however, for a faint streak, both sides are certainly deflected as if positive, though one slightly less than the other. As the amount of salt present is increased, the deflexion of the negative side (side towards the positive electrode) does not increase much, although, as already remarked, the deflexion of the positive side rapidly increases: the streak is broadened out. With large amounts of salt we get a plainly marked negative deflexion, but the negative part is always considerably smaller than the positive. The streak is forked above.

Thus there is no doubt that we can get negatively-charged luminous metallic atoms in the flame, just as we can in canal rays[†]. This can be explained, remembering that the electrons which are freed in the strongly positive side of the streak wander towards the negative side; hence the concentration of negative electricity grows from the positive to the negative side, and the probability of an atom being positively charged decreases. If there is only a little metal present, then firstly the streak is narrow, and secondly there are few free electrons. But if much metal is vaporized, then, with the broad streak and the many free electrons which wander through it, we may have large differences of concentration between the two sides of the streak, until finally, many metallic atoms in the negative side may become negatively charged for a fraction of the time.

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[*] G. Ebert, Heidelberg Dissertation, 1911.

[†] The atoms here spoken of are those forming the coloured streak: it has been shown elsewhere that some of the invisible negative carriers which are driven out of the streak, and detected on a strip outside the flame, are metallic. (E. N. da C. Andrade, Phil. Mag. June 1912, p. 865.)

§ 3. *Methods of Measuring the Conductivity.*

The method first adopted for measuring the conductivity was to bring two small parallel electrodes of platinum-foil into the body of the metallic vapour, and to measure the current sent through this resistance by potentials of from 0 to 100 volts. With a given amount of salt vaporized, the curve of current against potential was found to be of parabolic form, as has already been shown by Wilson [*]. As this form of curve does not offer readily a constant which measures the conductivity, this method was abandoned.

The electrodes were then made larger and placed further apart, usually at a distance of about 1·2 cm., their dimensions being 0·8 × 2 cm. The vapour was introduced between the electrodes as a luminous streak from a small bead; it did not touch either electrode. In this case the curves of current against voltage are straight lines, or Ohm's law holds within the observed limits, and a definite conductivity may be attributed to the salt-vapour for a given portion of the streak. The current spoken of above is the difference of the current through the pure flame, and the flame containing the salt. The curve of current against voltage for the pure flame is roughly parabolic.

Although we thus get a definite conductivity for a given position of the streak between the electrodes, this conductivity is changed by changing the position of the luminous streak relative to the electrodes, although these be kept fixed at a constant distance apart. As we bring the streak nearer to the negative electrode the current rapidly increases; if the vapour is in visible contact with the glowing electrode the current becomes comparatively enormous. The curves in fig. 1 show this effect. The abscissæ are the distance of the mid-line of the streak from the positive electrode; the electrodes were 1 cm. apart, and the streak roughly 4 mm. broad.

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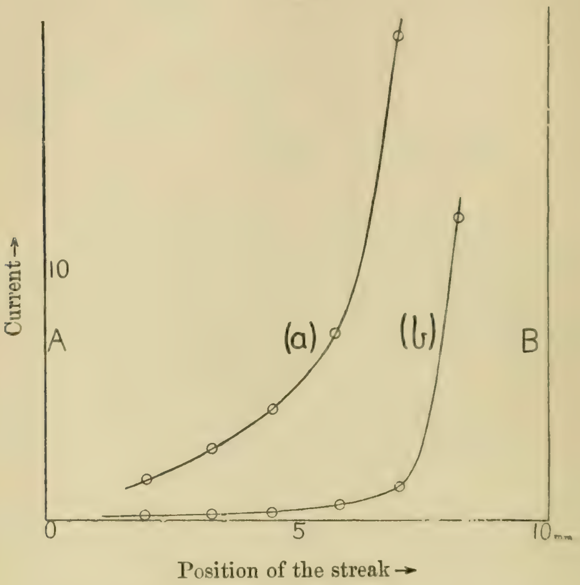
[*] H. A. Wilson, Phil. Mag. [6] x. p. 476 (1905).

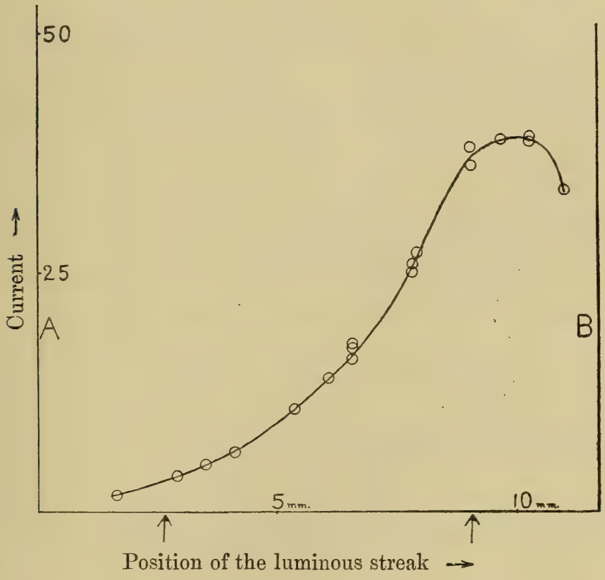
Fig. 1.



The ordinates are the current in arbitrary units (galvanometer deflexion); in order to show the great increase when the streak of vapour is in good contact with the negative electrode the curve (*b*) is given; the point on the extreme right corresponds to contact. The ordinates are $\frac{1}{10}$ the scale of the curve (*a*). Thus to obtain an estimate of some absolute measure of the conductivity this method cannot be used, as the glowing negative electrode produces a very disturbing effect.

To avoid the complication caused by the interaction of the glowing platinum and the vapour, experiments were made with an electrode kept artificially cool. The electrode was made of flattened brass tube, through which a constant circulation of cold water was kept up. This electrode was well in the flame, but, nevertheless, kept quite cool: it was earthed, and the other electrode kept at a known positive potential by means of a battery of small accumulators, one pole of which earthed, and the other connected to the electrode through a galvanometer. This electrode was a platinum strip, as before, since no anomalous effect was found at the positive electrode. On displacing the streak of vapour now from the positive towards the negative electrode the current increases, but on contact of the vapour with the negative electrode there is no abnormal effect, and if the luminous streak be still further displaced in the same direction (*i. e.*, so that only part of the streak lies between the electrodes) the current decreases, as we should expect. We thus have a perfectly definite maximum corresponding to the streak just touching the cooled negative electrode: the type of curve obtained is shown in fig. 2. It will be seen that the maximum is perfectly definite, and the glowing positive electrode exercises no abnormal influence.

Fig. 2.



The form of the curve and the maximum when the streak is in contact with the negative electrode is explained by the fact that the positive carriers have a very small velocity as compared with the negative. Consequently, if the streak is not in contact with the negative electrode, nearly the whole fall of potential takes place between the streak and the negative electrode. When the streak touches the negative electrode the small velocity of the positive carriers has little effect, as they have only a short distance to travel.

§4. *Calculation of the number of Free Electrons in the Metallic Vapour.*

If we assume a given velocity per unit gradient for the negative carriers of the flame we can calculate from the current they convey their number, since we know the charge per electron. We know also the number of metal atoms in a given volume of the Sr vapour, since we know from experiment the rate of vaporization for a given brilliancy *. Hence we can find the number of free electrons per Sr atom, or assuming that these are produced by the loss of an electron from a Sr atom, the fraction of the time during which the atom is positively charged.

To get the velocity of the electron we must know the potential gradient in the flame. The distribution of potential was found by measuring the difference of potential between the positive electrode and a parallel fine platinum wire inserted in the flame, the position of which could be regulated by a screw. The gradient was found to be very great by the negative electrode and gradually diminished towards the other electrode. If the electrons had the same velocity in all parts of the flame, the potential gradient ought to be uniform. But the cold negative electrode cools the flame in its neighbourhood strongly, so that probably the electrons only possess the velocity per $\frac{\text{volt}}{\text{cm.}}$ which they normally have, and which Wilson † has measured, at some distance from it, *i. e.*, near the positive electrode. We therefore take as the potential gradient in question the gradient near the positive electrode, and calculate the velocity of the electrons from it.

We take a case where the brightness of the streak, measured as described later, was 1·88 arbitrary units. In this case the potential fall per cm. near the positive electrode was $6 \frac{\text{volt}}{\text{cm.}}$.

Weight of SrO vaporized $= 0{\cdot}15$ mg. per hour,
$= 4 \times 10^{-8}$ gm. per sec.
Height of the electrode $= 0{\cdot}8$ cm.
Velocity of flame $= 450 \frac{\text{cm.}}{\text{sec.}}$

∴ Weight of metallic Sr in a portion of the streak

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* See § 7.

† H. A. Wilson, Phil. Trans. A. cxcii. p. 499 (1899).

0·8 cm. long

$$=\frac{88}{104}\,\frac{0{\cdot}8\times4\times10^{-8}}{450}\text{ gm.},$$

and the number of atoms in the given space

$$=\frac{88}{104}\,\frac{0{\cdot}8\times4\times10^{-8}}{450\times22\times10^{-23}}$$

$$=2{\cdot}8\times10^{11}\text{ atoms.}$$

Maximum deflexion of galvanometer $=18$ cm., and 1 cm. deflexion corresponds to a current of $2{\cdot}88\times10^{-8}$ amp.

Potential gradient near positive electrode $=6\ \frac{\text{volt}}{\text{cm.}}$.

We assume that the velocity per $\frac{\text{volt}}{\text{cm.}}$, v, of the electrons in the flame is $1000\ \frac{\text{cm.}}{\text{sec.}}\Big/\frac{\text{volt}}{\text{cm.}}$, as found by Wilson.

Let the number of free electrons produced per sec.

$$=n.$$

The elementary charge $=e$

$$=4{\cdot}7\times10^{-10}\text{ c.g.s. electrostatic (Planck).}$$

Then the current $=18\times2{\cdot}88\times10^{-8}$ amp.

$$=18\times2{\cdot}88\times3\times10^{9}\text{ c.g.s. electrostatic.}$$

But the current also $=nev$

$$=n\times4{\cdot}7\times10^{-10}\times6\times1000.$$

Equating these expressions for the current, we get

$$n=5{\cdot}5\times10^{8}\text{ electrons,}$$

while we have already found that the corresponding number of metallic atoms is $2{\cdot}8\times10^{11}$.

$\therefore$ each atom is positively charged $\frac{5{\cdot}5\times10^{8}}{2{\cdot}8\times10^{11}}$,

$$=\frac{1}{500}\text{ of the time.}$$

According to the velocity of migration of the positive carriers, as given by the deflexion of the luminous streak, this fraction is $\frac{1}{320}$, as the velocity of a permanently charged Sr atom should be $16\ \frac{\text{cm.}}{\text{sec.}}$*, and the velocity as obtained from the deflexion of the streak (of the given brightness) is $0{\cdot}05 \; \frac{\text{cm.}}{\text{sec.}} \Big/ \frac{\text{volt}}{\text{cm.}}$.

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* See E. N. da C. Andrade, "On the Nature and Velocity of Migration of the Carriers of Electricity in Flames, &c.," Phil. Mag. June 1912, p. 865.

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The rough agreement of these numbers is a satisfactory confirmation.

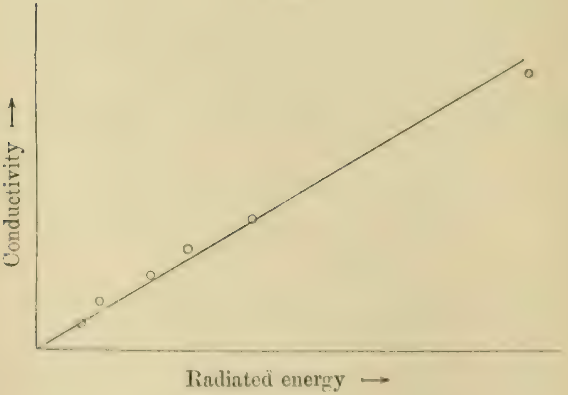
§ 5. *Relation between Conductivity and Light-emission.*

As in the previous experiments it was necessary to have some means of judging if the rate of vaporization of the salt remained the same in the different experiments, the brightness of the streak was measured with an optical pyrometer, as described in § 7.

Since no direct comparison of the light emission and conductivity seems to have been made, a brief series of experiments were made on this point. The luminosity of the coloured streak was varied by bringing different amounts of salt into the flame, and was measured with the pyrometer, the amount of energy radiated corresponding to the pyrometer readings being calculated as on p. 26. The conductivity was measured with a cooled negative electrode (see § 3), and the maximum current, *i. e.* the current obtained when the luminous streak just touches the electrode, in each case taken as the measure.

Fig. 3 shows the relation obtained between radiated energy and conductivity. They are roughly proportional. The measurements are exhibited in the following table :—

Fig. 3.



Difference of potential between the electrodes = 100 volts.

Pyrometer reading.	Radiated energy.	Conductivity.
1·98	2·60	37·0
1·88	1·15	18·0
1·85	0·80	14·0
1·82	0·60	10·5
1·78	0·35	6·5
1·76	0·25	3·5

All the measurements are in arbitrary units.

The conductivity of the pure flame, which was naturally always subtracted from the reading for the flame with salt, was about 5 arbitrary units.

The proportionality between conductivity and luminosity (radiated light energy) is to be expected from the known similarity between the laws connecting conductivity and concentration of metal in the flame, and connecting light-emission and concentration [*].

The fact that chlorine can destroy the luminosity of metallic vapours in flame without much influencing the conductivity [†], can be explained by the action of the glowing platinum electrodes, which, in the measurements in question, stood in the body of the vapour. It is probable that the impact of molecules of the chloride with one another is ineffectual in the liberation of electrons, which is effected by the impact of uncombined metallic atoms with one another : this accounts for the lack of light-emission. On the other hand, the impact of the chloride molecules on the glowing platinum may suffice to liberate electrons ; it is probable that the greater part of the conductivity is always due to liberation of electrons at the surface of the electrodes, when they stand in the vapour (see the experiments in § 3). For a fuller discussion of these views see a paper by P. Lenard [‡].

I propose making experiments on the effect of chlorine on the conductivity of the vapour when the electrodes do not stand in the vapour itself, which should throw some further light on the matter.

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[*] See Arrhenius, *Ann. der Physik*, xlii. p. 18 (1891), and Gouy, *Ann. de Chemie et de Physique* [5] xviii. p. 1 (1879).

[†] Smithells, Dawson, and Wilson, Phil. Trans. A. cxciii. p. 89 (1900).

[‡] P. Lenard, *Sitzungsberichte der Heidelberger Academie*, Dec. 1911.

§ 6. *Apparatus for the experiments at High Pressure.*

The colourless flame of air and gas burnt from a flat quartz flame-piece between two thick brass electrodes standing outside the flame: the bead of salt could be brought at will into the flame by a small magnetic arrangement. The disposition of the apparatus was much as described elsewhere [*], the same burner, electrodes, and influence machine being used. The flame, however, burnt in a closed vessel, in which the pressure could be varied from atmospheric to six atmospheres; the vessel was made in cylindrical form of iron lined with copper, and was 40 cm. in diameter and 60 cm. high; the top and bottom were removable, being bolted on with screws and nuts; the joints were made air-tight with thick rubber rings. In the bottom of the vessel were an inlet for gas and two for air, one being to supply the burner with air, and the other to keep the air in the vessel constantly renewed. Insulating plugs in the bottom of the vessel bore the wire to the insulated electrode, the wire for supplying the current to small magnet, and the two wires connected to the parallel "probes" of fine platinum wire used for measuring the fall of potential in the flame; in the last case the insulations were of amber. All the plugs were protected from dirt and moisture by brass caps. The flame was observed through a small plate-glass window. The cover of the vessel was provided with a pressure gauge and a cock to regulate the escape of air: this cock communicated with a copper chimney which came directly over the flame, and collected the foul air. The vessel was surrounded for two thirds of its height by a cooling jacket of thin tinplate, through which a constant circulation of cold water was maintained. The coal gas and air used were compressed in a neighbouring room by means of a small compression pump, and stored in large iron vessels at 10 atmospheres pressure, from which they were brought to the experimenting room through lead pipes.

The flame is lighted and the cover bolted on. Compressed air is then let into the vessel; as the pressure rises the supply of air and gas to the flame must be carefully increased, in order to keep the flame burning at a constant size. With a little practice the flame may be raised to a pressure of five atmospheres, and kept burning there for an hour or more. During experiments the cock in the cover must, of course, be partly open and a constant supply of fresh air maintained.

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[*] E. N. da C. Andrade, *loc. cit.* p. 867.

The appearance of the flame changes considerably with rise of pressure. The flame-piece used in these experiments was of quartz with a rectangular opening 11 mm. by 2 mm.; the hollow space of the flame (usually called the cone, though in this case it was nearly rectangular in shape) was always adjusted to the same height, about 1 cm. As the pressure is raised the outer edge of the flame becomes brighter than the rest of the flame, taking on the appearance of the bright blue line which defines the cone. At an excess pressure of about two atmospheres this outer line is very plainly marked, and the space bounded by it has somewhat shrunk together above, while outside the blue line the flame is seen in two horns. At higher pressures this appearance becomes more definite ; the outer blue line defines a more or less pointed space, and the two horns of pale blue flame become very definite : the flame has thus three points above. The inner part of the flame above the cone appears faintly reddish at high pressures (3–5 atmospheres) and gives a continuous spectrum. If a round flame-piece be used the same phenomena are observed, modified by the shape of the flame.

When the electric field is applied, the flame loses this distinctive appearance ; it appears to be to some extent depressed from above and broadens out : the different parts so clearly seen before become merged. The flame presents a uniform appearance, without projections, and though on the whole a little more deflected towards the negative than the positive electrode, it seems, by the broadening, to be deflected in both directions.

On bringing a platinum wire bearing a little salt into the flame, it was observed that with a fixed amount of salt on the wire the streak of coloured vapour appeared somewhat fainter at high pressures. It seemed possible that the same amount of salt vaporizing at high pressure might not radiate so intensely as at atmospheric. The other alternative is that the salt was not vaporizing so freely at high pressure. To test this point measurements were made of the amount of salt vaporized for a given luminosity at various pressures.

§ 7. *Measurements of the Luminosity of the Streak, and the Weight of Salt vaporized.*

The metal used was strontium, and to measure the brightness of the red streak of strontium vapour an optical pyrometer (Lummer and Kurlbaum type) was used, the observations being made through a red glass. By observation of the current required to make the filament in the instrument glow at the brightness of the luminous streak, so as to be invisible when against it, we can obtain the temperature of the "black body" which would radiate the given radiation with the observed intensity. Curves (by the Phys. Tech. Reichsanstalt) are supplied with the instrument which enables this to be read off directly. Knowing this we can calculate the relative amounts of energy radiated for two different readings. Using Planck's radiation formula

$$E = \frac{c\lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1},$$

we have

$$\frac{E_1}{E_2} = e^{\frac{c_2}{\lambda}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)},$$

where c_2 is a constant having the value 14200 if λ be expressed in μ, and T_1, T_2 are the "black-body" temperatures in the absolute scale.

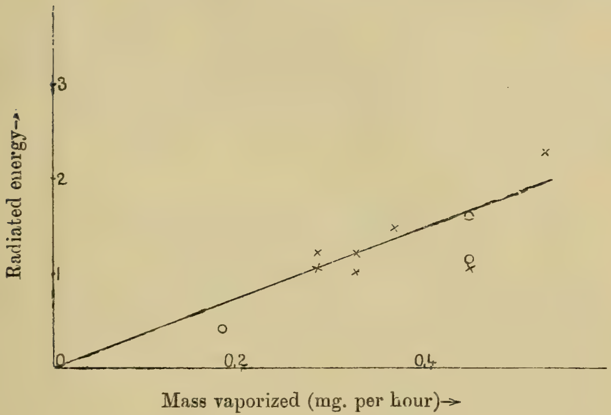
The amounts of salt vaporized are very small, fractions of a mg. per hour. A microbalance to weigh these amounts was constructed by fixing a light horizontal arm of aluminium at right angles on a stretched horizontal quartz thread. To one end of the arm a hook was hung by means of a very fine silk fibre, while at the other was a counterpoise, which caused the arm to rest against a stop when the balance was unloaded, while when the platinum wire was hung on the hook, the arm swung free. Readings were made with a horizontal microscope provided with a scale in the eyepiece: a whole scale-division (tenths could be read) corresponded to a change in weight of 0·2 mg. The whole was enclosed in an air-tight case and kept dry with P_2O_5.

The strontium salt ($SrCl_2$) was always glowed before the experiment, so as to be in the state of oxide, the wire of the loop being covered with a thin layer of salt; a bead of salt in the loop could not be used, as with so much salt the luminosity varies too quickly, and there is also danger of the mass breaking away partly from the wire. The wire was generally in the flame for an hour, observations with the pyrometer being made at regular intervals. The luminosity was altered from experiment to experiment by varying the small amount of salt on the wire (by prolonged glowing);

to compensate for the decreased diffusion, and consequent narrowing of the streak at high pressure, the effective size of the loop was increased by turning its plane towards the horizontal at high pressure, it being vertical at atmospheric pressure.

The results are shown in fig. 4, where the energy radiated

Fig. 4.



(obtained from the pyrometer readings in the way mentioned) is plotted against the weight of SrO (in mgs.) vaporized per hour. The energy is in arbitrary units, as only relative numbers can be obtained. The crosses refer to the measurements made at 1 atmosphere, the circles to those made at 4 atmospheres. The inaccuracies of measurement with such small weights of salt are necessarily large (10 to 20 per cent.), and unfortunately for the larger weights, where we hope for increased accuracy in the weighings, the radiated energy varies very rapidly with the pyrometer reading, introducing compensating uncertainty. We may, however, from these experiments safely conclude that at fourfold pressure the light-energy radiated by a given amount of vaporized salt is not changed by 25 per cent. ; it is probable that it does not vary with the pressure. Guoy * has found that for small amounts of salt the luminosity is proportional to the amount of salt vaporized. A straight line is therefore drawn through the origin and the mean of the points, to enable us to judge roughly what weight of metal

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* M. Guoy, *Ann. de Chim. et Phys.* (5) xviii. p. 1 (1879).

is required to produce a given luminosity, so that in further experiments the pyrometer reading gives approximately the rate of vaporization in mgs. per hour.

As the luminosity is roughly, at any rate, independent of the pressure for a given rate of vaporization of the salt, it was thought that the flame temperature might be lower at high pressure than at atmospheric, and that this might be the reason why the streak is somewhat paler at high pressure, with the same salted wire in the flame in each case. Measurements were made of the temperature of the flame at different points at different pressures by means of a platinum-platinorhodium thermocouple. It was found that the flame was on the average nearly 100° cooler at 4 atmospheres than at 1 atmosphere.

§ 8. *The Migration of the Positive Carriers at High Pressure.*

When the salt is brought into the flame at high pressure in a central position, the coloured streak follows the form of the flame, and is consequently divided into three points above. It is brightest in the central portion of the flame, and lighter at the sides.

When the electric field is applied these points merge, as stated in the last paragraph; the streak of luminous vapour is, however, always split into two in the electric field, showing the existence of both positively- and negatively-charged luminous metal atoms. At three atmospheres excess pressure, *e.g.*, if the bead is central the deflexion of the two parts are approximately equal, the positive and the negative streak being roughly equally bright. The deflexion of the flame alone is hard to estimate since it is broadened out (§7), and seems to be deflected to some extent in both directions. It was attempted to estimate the deflexion of the flame by bringing coal-dust particles into it, as was done to determine the flame velocity *, but this was unreliable, since the particles probably become charged.

The difficulty was got over by bringing the bead into the flame close to the edge nearest the negative electrode: the deflexion of this edge of the flame was taken as the deflexion of the flame at the region occupied by the streak of positively charged vapour. The deflexion of the positive edge of the streak of metallic vapour was observed, thus giving the maximum velocity of migration of the metallic atoms forming the luminous streak. The deflexions were read on a glass scale, the

* See p. 30.

salt being brought in and out of the flame, and readings for the pure flame and the streak of vapour made alternately at each pressure. The flame was always adjusted as nearly as possible to the same size; the brightness of the streak was measured at each pressure by the pyrometer, and the potential of the insulated electrode read. The luminosity was kept approximately constant at all pressures by adjusting the amount of salt on the wire; the experiments at highest pressure were done first, since, as mentioned, the salt does not vaporize quite so readily here.

Series of experiments over the range of pressures were made with two different luminosities, *i. e.*, rates of vaporization. As already mentioned (§2), the deflexion of the streak depends upon the rate of vaporization of the salt, decreasing with decreasing rate, but reaching a constant small value for amounts of salt below a certain limit. For one series of experiments the rate was kept within this limit, for the other a much greater constant rate was used, giving a deflexion in the electric field three or four times as great. The deflexion of the faint streak was not more than 5° greater than that of the pure flame; hence in some measure it furnishes a check upon our estimate of the deflexion of the pure flame at high pressure. It is found that whether we subtract the deflexion of the faint streak, or the deflexion of the pure flame estimated as described above from the deflexion of the stronger streak, we have the same result:—that with constant potential of the insulated electrode and constant size of the flame the deflexion of the luminous streak is approximately the same over the range of pressure 1 to 4 atmospheres. The following table exhibits this:—

TABLE I.

Deflexion of the stronger streak.

Pressure (Atmospheres).	Flame angle θ.	Streak angle. a.	Pyrometer (arb. units).	$a-\theta$.
4·05	13°	32°	1·98	19°
3·9	12°	28°	1·80	16°
3·9	13°	34°	1·88	21°
3·8	14°	33°	1·92	19°
3·15	13°	33°	1·94	20°
2·55	13°	30°	1·94	17°
1·9	13°	30°	1·94	17°
1·3	18°	36°	1·90	18°
1·0	14°	33°	1·92	19°

Deflexion of the weaker streak.

Pressure.	Streak angle. a'.	Pyrometer.	$a-a'$.	$a'-\theta$.
4·4	17°	About 1·72. But	15°	4°
3·9	16°	for such small	18°	4°
3·2	16°	luminosities	17°	3°
2·35	17°	the instrument	16°	4°
2·05	17°	is unreliable.	14°	
1·3	17°		19°	
1·0	17°·5		15°·5	3·5°

To find the true velocity of migration per $\frac{\text{volt}}{\text{cm.}}$ we must know the potential gradient in the flame, and the flame velocities. The latter were measured by bringing small carbon particles into the flame, and observing it in a rotating mirror *. The flame velocity diminishes linearly with increasing presure; the relation is exhibited in fig. 5 (*a*). The fall of potential in the flame was measured by bringing two fine parallel platinum wires into the flame, and measuring the potential difference between them with a calibrated aluminium leaf electrometer; two different distances of the fine wires were employed. The potential gradient in the flame increases with the pressure when the potential of the insulated electrode is kept constant: this is to be expected, since the conductivity of the flame decreases very rapidly with increasing pressure. The variation of the gradient in a flame of fixed size with the pressure, the potential difference between the electrodes being constant, is shown in fig. 5 (*b*). From the angle of deviation of the streak and the curves (*a*) and (*b*) of fig. 5, the dependence of the velocity of migration of the positive carriers of the luminous streak upon the pressure can be calculated. The experimental numbers are shown in the following table (II.); they refer to the stronger streak.

The product $v \times$ pressure, exhibited in the last column of the table, is roughly constant; the variations are not larger than are to be expect d from unavoidable errors in the different measurements. Thus from 1 to 4 atmospheres the velocity of migration is inversely proportional to the pressure: the experimental curve connecting these quantities is shown in fig. 5 (*c*).

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* For detail of the method see E. N. da C. Andrade, *Ann. der Physik* (4) xxxvii. p. 380 (1912).

Fig. 5.

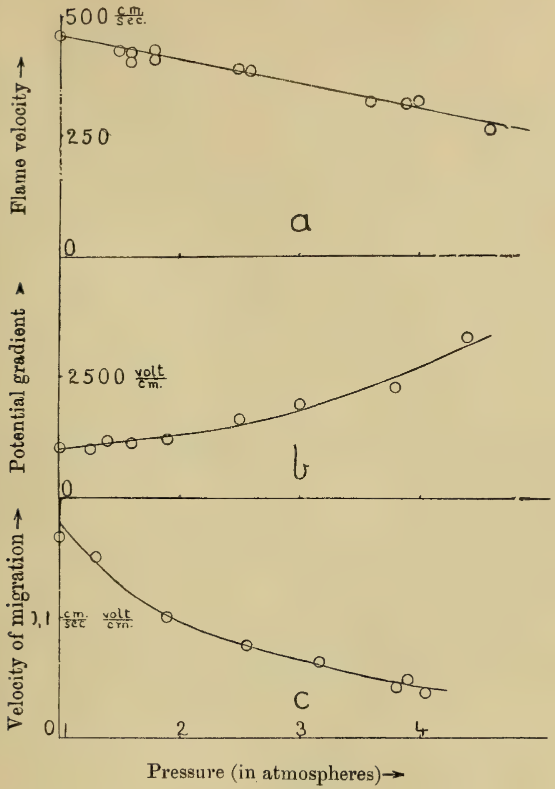

Table II.

Velocity of migration and pressure.

Pressure (Atmospheres).	Potential gradient (volt/cm.).	Flame velocity cm./sec.).	$a-\theta$	tan $(a-\theta)$.	Velocity of migration $=v$.	$v\times$pressure.
1	950	460	19°	0·344	0·166 $\frac{\text{cm.}}{\text{sec.}}\Big/\frac{\text{volt.}}{\text{cm.}}$	166
1·3	1000	445	18°	0·325	0·130	170
1·9	1260	415	17°	0·305	0·100	190
2·55	1550	380	17°	0·305	0·75	190
3·15	2000	345	20°	0·364	0·63	198
3·8	2500	310	19°	0·344	0·42	160
3·9	2600	300	23°	0·424	0·49	191
4·05	2700	290	19°	0·344	0·37	150

§ 9. *Experiments at Reduced Pressures.*

This result renders doubtful the work of G. Ebert[*], who carried out experiments at low pressures (76 to 26 cm. Hg) and found that in this range the velocity of migration is independent of the pressure. But he records that the potential gradient in the flame *rises* with decreasing pressure, which is highly improbable, in view of the well-known increased conductivity of gases at lower pressures[†]. It therefore seemed advisable to repeat the experiments at low pressure. The flame and electrodes were those used in the high-pressure experiment: they stood on a smooth plate provided with the necessary inlets for gas and air, and were covered by a large bell-jar, which could be rapidly exhausted by means of a large oil pump, which was kept running continuously. The platinum wires used to measure the potential difference in the flame were 0·2 mm. in diameter, and experiments were done with them at two different distances from one another (6·4 mm. and 5·1 mm.). If a luminous streak of the metallic vapour be brought between them, not touching either, there is no perceptible change in the difference of potential between them, provided the streak is not too strong. We can therefore measure the difference of potential in the flame itself.

It was first shown that the potential gradient in the flame was proportional to the potential of the insulated electrode, as was to be expected. This indicates that the wires were giving reliable measurements of the gradient: Ebert's measurements are very discordant on this point, and seem to indicate experimental errors[‡].

The pressure was then varied. With a constant potential of the insulated electrode the gradient in the flame decreased rapidly with decreasing pressure.

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[*] G. Ebert, Heidelberg Diss., 1911.

[†] There are also contradictions in the measurements recorded in Ebert's paper which point to the measurements of potential gradient being unreliable.

[‡] It appears that Ebert made measurements without varying the distance apart of the probe wires, the fixed distance used by him being very small (2 mm. or less). With so small a distance, especially if the wires are not very thin, there may be many disturbing influences: the flame between the wires is much cooled, and possibly some kind of a mutual action takes place between the wires, which action would probably extend to greater distances with decreasing pressure. I tried to measure with a very small distance apart (1·5 mm.) and could get no satisfactory results.

Difference of potential between electrodes 11,000 volts.

Distance apart of electrodes 5·5 cm.

Distance apart of probe wires.	Pressure.	Potential gradient in flame.
6·4 mm.	76 cm. Hg.	1160 $\frac{\text{volt}}{\text{cm.}}$
6·4 ,,	50 ,,	840 ,,
6·4 ,,	30 ,,	590 ,,
5·1 ,,	76 ,,	1110 ,,
5·1 ,,	28 ,,	400 ,,

From these experiments we have the variation of the gradient of potential in the flame at reduced pressures. The deflexion of the streak remained about constant when the potential of the insulated electrode was constant, as found by Ebert. The velocity of the flame was not actually measured: according to Ebert it varies only slightly with the pressure in this range, and extrapolation of my measurements at high pressure gives a variation of less than 10 per cent. in the given range. From these results the velocity of migration at low pressures was calculated.

Pressure.	Velocity of migration.	Product.
76 cm. Hg.	90 arbitrary units.	684
50 ,,	120 ,, ,,	600
30 ,,	200 ,, ,,	600

The velocity of migration is again inversely as the pressure. Thus from 30 cms. Hg to 4 atmospheres the velocity of migration of the positive carriers of the first kind * is inversely proportional to the pressure.

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* See E. N. da C. Andrade "On the Nature and Velocity of Migration of the Carriers of Electricity in Flames," Phil. Mag. June 1912, p. 866.

§ 10. *Relation between Conductivity and Pressure.*

The experiments on conductivity were made with a streak of metallic vapour (strontium) as described in § 3: the electrodes, of platinum foil, were 1·2 cm. apart, and the streak stood between them, without touching either. As only the alteration of the current is here required, the action of the glowing negative electrode produces no disturbance, when we consider that it was shown that at atmospheric pressure *for this position of the streak* the current is almost the same for a hot as for a cold negative electrode. The galvanometer was read first with the streak present, and then for the pure flame, and the difference of the readings taken as proportional to the conductivity of the salt vapour.

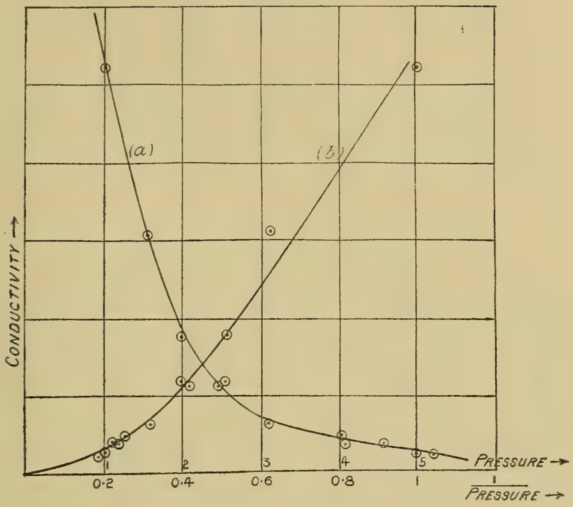
It has already been shown (§ 3) that, if the whole streak lies between the electrodes, without touching them, the current is proportional to the applied potential in the experimental range of 0 to 100 volts. Measurements were therefore made mostly for one fixed potential difference, 100 volts. The results are exhibited in the following table:—

TABLE III.

Pressure (Atmospheres).	Conductivity (arbitrary units).	Pressure × conductivity.
1	10·4	10·4
1·6	6·2	9·3
1·95	3·6	7·2
2·4	2·3	5·5
2·55	2·4	6·1
3·1	1·3	4·0
4·0	0·80	3·2
4·05	0·80	3·2
5·0	0·55	2·75
5·2	0·50	2·6

The relation between conductivity and pressure is shown in fig. 6 (*a*). From curve (*b*), where the conductivity is shown against the reciprocal of the pressure, it is to be seen that the conductivity diminishes faster than it would if it were proportional to the reciprocal of pressure. The cause of this may possibly be the fact that the diffusion is very much greater at atmospheric pressure. This makes it possible that at atmospheric pressure some of the metal atoms diffuse as far as the negative electrode, which would make the current too great. The number need not be large, since the mutual action between metal atoms and the glowing electrode is so great (§ 3).

Fig. 6.



§ 11. *Theoretical.*

The general result of measurements extending over a range of pressure of 0·4 to 4 atmospheres is that the velocity of migration of positive metallic carriers of the first kind is inversely as the pressure. Now, according to all formulæ for the mobility of a charged atom in a gas *, the mobility is inversely as the pressure of the gas. Hence we conclude that the fraction of time during which a metallic carrier is positively charged is independent of the pressure.

This leads us to the conclusion that the liberation of the electron from the metallic atom is, mainly at least, effected by the impact, or rather, perhaps, the action at short distance (Nähewirkung) of metal atom on metal atom. For the number of these impacts remains constant with varying

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* *E.g.* the formula given by Lenard (*Ann. der Physik* (4) iii. p. 313 (1900)) for the mobility of a charged carrier of atomic size,

$$\omega = \frac{3}{2\pi\sqrt{2}} \frac{eF}{Ds^2W},$$

where s is the sum of radii of carrier and gas molecule,

D is the density of the gas,

W is the mean velocity of the gas molecule.

pressure, whereas the number of impacts of metal atoms with molecules of the flame gases increases with increasing pressure. But whereas metal atom with metal atom is the chief cause of the liberation of the electron, it is probable that the impact with a gas molecule is, to a relatively very small extent, capable of freeing an electron under favourable circumstances, since with decreasing rate of vaporization of the metal we reach a fixed small limiting value of the deviation of the luminous metallic vapour in an electric field. Only brief reference is made to these points here, since the whole question has recently been fully discussed by Lenard *.

§ 12. *Conclusions.*

1. Negatively-charged luminous metallic carriers can exist in a flame, in addition to the known positive carriers.
2. If a streak of metallic vapour stand between, but not touching, two electrodes in the flame, Ohm's law holds for the conductivity of the vapour within the observed range.
3. If a cooled negative electrode be employed, with a given voltage a definite maximum current is obtained on displacing a luminous metallic vapour streak between the electrodes towards the negative electrode in the flame. An estimate of the number of free electrons produced per second in the streak may be obtained from this.
4. The conductivity and energy of light-emission of a streak of metallic vapour are proportional within the observed range.
5. The energy of light-emission for a given rate of vaporization of metal is roughly independent of the pressure.
6. The velocity of migration of the positive carriers of the luminous streak is inversely proportional to the pressure, and hence the fraction of the time during which a carrier is positively charged is independent of the pressure. This leads to the theoretical conclusion that the impact of metal atom against metal atom is the main cause of the liberation of an electron from a metal atom.

It gives me great pleasure to thank here Prof. P. Lenard, in whose Institute at Heidelberg these experiments were carried out, for his constant advice and encouragement, and for his great kindness throughout the work. To Dr. Ramsauer I am also indebted for much assistance in the course of the work.

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* P. Lenard, *Sitzungsberichte der Heidelberger Acad.* 1911, "Ueber die Elektricitätsleitung und Lichtemission metallhaltiger Flammen."

III. *On the Asymmetry in the Distribution of Secondary Cathode Rays produced by X-Rays; and its Dependence on the Penetrating Power of the Exciting Rays.* By C. D. Cooksey, *Ph.D., Instructor in Physics, Sheffield Scientific School, Yale University*[*].

IT has been shown by Bragg and Madsen[†] that the amount of secondary β radiation excited in various solids by γ-rays is not symmetrically distributed about a plane perpendicular to the direction of propagation of the γ-rays, but that the β radiation which comes from the side from which the γ-rays emerge is greater than that coming from the side on which the γ-rays are incident. The same effect is observed, though to a less degree, in the case of secondary X-rays[‡], and the secondary cathode rays produced by X-rays[§], and those produced by ultra-violet light[||]. This lack of symmetry is less for soft γ-rays than for hard and still less for X-rays, which are usually considered as very soft γ-rays. The order of magnitude of the ratio of emergence to incidence radiation ranges all the way from 20 : 1 down to unity, depending on the nature of the radiations used and the substance in which the secondary rays are excited.

Since I first showed that this effect was true for the cathode rays produced by X-rays, I have been experimenting with a view to find how the ratio of emergence to incidence radiation depends on the hardness of the exciting rays. But with these rays the effect is so small at best that the variations which might be produced by the widest possible variation in hardness of the primary are not likely to be much greater than the experimental errors always inherent in X-ray measurements. Some results which I at first obtained[¶] seemed to indicate that there was a slight increase in the ratio with an increase of hardness of the primary. But owing to the heterogeneity of the rays from an ordinary tube, and the difficulty, at that time, of sorting out and using rays of a single penetrating power, these results were not very convincing.

Since these results were obtained, however, the work of Prof. Barkla and others on "Fluorescent" X-radiations, a summary of which is to be found in the Phil. Mag. for Sept. 1911, page 396, has afforded a convenient means of obtaining homogeneous beams of X-rays of known penetrating powers over a wide range. It was by this means that the experiments described in the present paper were performed.

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[*] Communicated by the Author.

[†] Trans. Roy. Soc. South Australia, vol. xxxii. May 1908.

[‡] Bragg & Glasson, *loc. cit.* Oct. 1908.

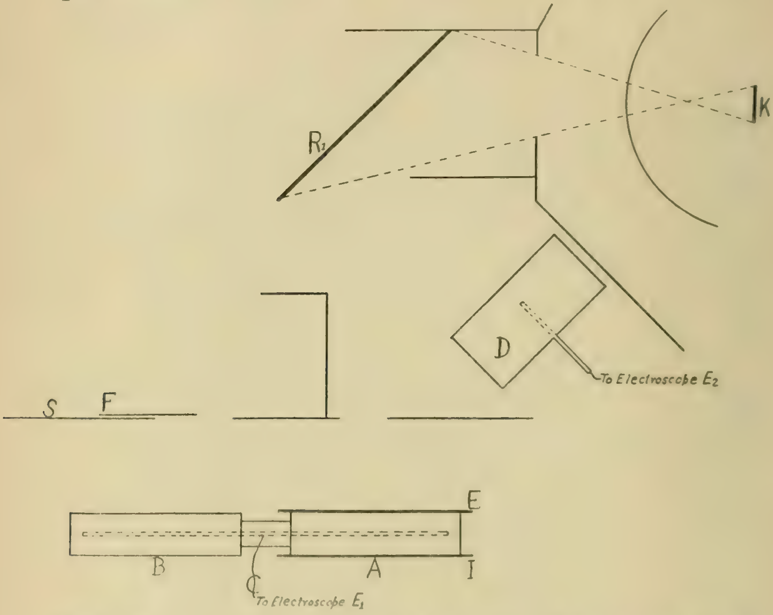
[§] Cooksey, 'Nature,' vol. lxxvii. p. 509 (1908).

[||] Stuhlmann, Phil. Mag. vol. xxii. p. 854 (1911).

[¶] 'Nature,' vol. lxxxii. p. 128 (1909).

Apparatus and Method.

The apparatus used is shown in the accompanying diagram and was a modified form of the apparatus used in previous experiments*.



The X-ray tube was completely enclosed in a thick lead box, and the rays, proceeding from the anti-cathode, K, passed through a window in the box and fell on the radiator, R$_1$, which consisted of a metal known to give off fluorescent X-rays. The fluorescent rays from R$_1$ passed through windows in a lead screen, S, into the ionization-chambers, A and B, which were maintained at potentials of +240 and −240 volts respectively. A wire, C, passing into A and B through insulating plugs was connected to the gold leaf of a sensitive electroscope, E$_1$, of the type described by R. T. Beatty †. The two quadrants of this electroscope were connected to A and B respectively, and the wire C was normally connected to earth. A third ionization-chamber, D, received some of the rays from R_1 and was always connected to earth. A wire running from the inside of D and insulated from it connected with the gold leaf of a second electroscope, E_2, of the ordinary type. This wire and gold leaf could be charged to any convenient potential; and the rate of fall of the gold leaf when the rays were turned on served as a measure of the intensity of the rays from R_1. Each electroscope was fitted with a microscope and scale for observing the motion of the gold leaf. A lead screen, F, could be slid across the window in front of B by means of a screw, giving a very fine adjustment of the amount of the radiation entering this chamber.

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* Am. Jour. Sci. vol. xxiv. p. 285 (1907).

† Phil. Mag. vol. xiv. p. 604 (1907).

The chambers A and B consisted of brass cylinders about 10 cm. in diameter and 2·2 cm. long, covered with lead on the outside. The ends of B were covered with aluminium foil. The end of the wire C which entered A terminated in a wire ring of a diameter slightly less than the inside diameter of A, and lying in a plane perpendicular to the axis of A. The opening in the screen S opposite A was so adjusted that no part of the beam from R_1 could fall on the ring or on the walls of A.

Brass plate-holders, E and I, covered the ends of A. These plate-holders were made exactly alike to be interchangeable. Each one consisted of two square brass plates, held together with screws, and having a circular hole bored through their centre of about the same diameter as the inside of A. These plate-holders could be slid on and off the ends of A in somewhat the same manner as a camera plate-holder, and stops were so placed that they would always come to the same position, with the centre of the hole on the axis of A.

In order to produce the emergence cathode rays it was necessary to pass the rays from R_1 through a plate of some metal in which cathode rays are produced in sufficient numbers to be easily measured. As these metals are relatively opaque to X-rays it was necessary to use very thin sheets. Gold and silver were fixed upon for this purpose. The gold leaf was $0{\cdot}8 \times 10^{-5}$ cm. thick and the silver leaf $1{\cdot}8 \times 10^{-5}$ cm. Circular disks of aluminium about 0·012 cm. thick were made with a diameter slightly larger than the holes in the plate-holders, and on one side of each was laid a thin foil of one of the above metals, stuck on with a thin coat of vaseline. When thicker sheets of metal were wanted more foils could be added by first holding the disks, already covered with one foil, in the vapour of heated vaseline, and then laying them on the foil to be added. One of these disks covered with one of the metals, say gold, was then screwed between the two parts of each plate-holder and the holders placed over the ends of A with the aluminium sides facing in.

When the tube was turned on, and the wire C insulated from the earth, there would be a motion of the gold leaf in the electroscope E_1 toward one or other of the quadrants depending upon whether the ionization in A or B was more intense. By a suitable adjustment of the screen F the ionization in the two chambers could be made equal, when there would be no motion of the gold leaf. After this adjustment was made the tube was stopped, and the front holder E reversed so that the gold side faced into A. The leaf in the electroscope E_2 was then charged to a potential of about 200 volts, and the tube again excited. When the leaf reached a certain division on the scale the wire C was again insulated, and after the leaf in E_2 had passed over a convenient number of scale-divisions the tube was stopped. The position of the leaf in E_1 was then observed, and C connected to earth through a potentiometer, and a sufficient potential applied to keep the leaf at its observed position. Calling this potential a, we can take it as a measure of the excess of ionization in A over that in B. If e denote the ionization produced by the emergence secondary rays from the gold, and e' that by the emergence secondary rays from aluminium, we shall have

$$e - e' = ka,$$

where k is a constant.

After this measurement was made the holder E was turned back with the aluminium face in, and the other holder I reversed so that the gold faced in. The tube was again excited, and the potential b acquired by the leaf in E_1 while the leaf in E_2 passed over the same interval as before was measured. Denoting the ionization produced by the incidence secondary rays from the gold by i, and that by the incidence secondary rays from the aluminium by i', we can write as before

$$i - i' = kb.$$

Letting $e'/e = m$, and $i'/i = n$ we shall have

$$e/i = a/b(1 - n)/(1 - m);$$

where e/i is the ratio of the emergence secondary radiations produced in the gold by a certain beam of X-rays from R_1 to the incidence secondary radiations produced by the same beam after traversing the ionization-chamber. In the light of the results obtained in a previous paper*, and owing to the fact that the ionization-chambers used in the present work were only two fifths as long as those used before, we may assume that the secondary X-rays from the metal produced a negligible amount of ionization in the chamber compared with that produced by the cathode rays from the metal.

No data are readily obtainable in regard to m, but it is known that the amount of cathode rays given out by aluminium is very small compared with the amount given out by metals of high atomic weight such as gold and silver. Unless the ratio of emergence to incidence radiation is far different in aluminium from what it is in gold and silver, which is unlikely, the difference between m and n will be a quantity which we may neglect, and we may write for a sufficient approximation

$$e/i = a/b.$$

The determination of e/i, as above described, was always repeated with the two plate-holders reversed with respect to the ends of A, which should give the same result if both plates were the same. The values obtained, however, in the two cases differed very widely; much more than could be accounted for by the experimental errors. The only explanation seemed to be that, owing to dirt on the surface or variations in the thickness of the metal foils, one plate was more efficient in giving out cathode rays than the other. If this were the case both the incidence and emergence rays should be affected in the same ratio, and the geometric mean of the two determinations of e/i should give the same result. To test this different pairs of plates were made and also more foils were added to the same plates, but no matter what the discordance was between the two values of e/i for a given pair of plates, the geometric mean of the value found when one plate was on the front of A and the other on the back, and the value when these positions were reversed, always gave the same result within the limits of error of the experiment.

This ratio e/i does not, however, give the true ratio of emergence to incidence effect for the same intensity of exciting rays, owing to the fact that these were absorbed in the air of the ionization-chamber and to some extent in the layer of the metal from which the cathode rays come. The ratio of the number of emergence cathode rays coming from a layer of the metal so thin that the exciting rays suffer no absorption in it to the number of incidence cathode rays coming from the same layer is the true value sought. Let this be designated by R. Let β be the coefficient of absorption of the cathode rays in the metal from which they come, λ_1 the coefficient of the exciting X-rays in the same metal, and λ_2 their coefficient in air. The number of emergence cathode rays produced in a layer of thickness dx at a depth x of the metal by X-rays of intensity I is equal to

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* Am. Jour. Sci. vol. xxiv. p. 285 (1907).

$$\mathrm{K\,I}\,dx,$$

where K is some constant. If the intensity of the X-rays on entering the metal is I_0, and the thickness of the plate t, the number of the emergence cathode rays which get out of this layer into the ionization-chamber is equal to

$$\mathrm{K\,I}_0\epsilon^{-\lambda_1 x}\epsilon^{-\beta(t-x)}dx,$$

and the total number getting out of the whole plate is

$$e=\mathrm{K\,I}_0\epsilon^{-\beta t}\int_0^t \epsilon^{(\beta-\lambda_1)x}dx$$

$$=\frac{\mathrm{K\,I}_0\epsilon^{-\beta t}}{\beta-\lambda_1}\left[\epsilon^{(\beta-\lambda_1)t}-1\right].$$

The X-rays after being absorbed in the plate on the front of A are absorbed by the air in A and by the plate on the back of A. Therefore the intensity of these rays after reaching a depth x of the second plate will be

$$\mathrm{I}_0\epsilon^{-\lambda_1 t}\epsilon^{-\lambda_2 t'}\epsilon^{-\lambda_1 x},$$

where t' is the length of the ionization-chamber. Therefore the number of incidence cathode rays getting into the ionization-chamber from the second plate of thickness t will be equal to

$$i=\frac{\mathrm{K\,I}_0\epsilon^{-(\lambda_1 t+\lambda_2 t')}}{\mathrm{R}(\beta+\lambda_1)}\left[1-\epsilon^{-(\beta+\lambda_1)t}\right].$$

The ratio of the number of emergence cathode rays entering A to the number of incidence cathode rays is therefore

$$e/i=\mathrm{R}\frac{\beta+\lambda_1}{\beta-\lambda_1}\epsilon^{2\lambda_1 t+\lambda_2 t'}\left[\frac{\epsilon^{(\beta-\lambda_1)t}-1}{\epsilon^{(\beta+\lambda_1)t}-1}\right].$$

Since λ_1 is small compared with β, the most important part of this equation is $R\epsilon^{\lambda_2 t'}$. Designating the other factors by S we may write

$$R = \frac{e/i}{S\epsilon^{\lambda_2 t'}}.$$

If we assume that the absorption coefficient of the cathode rays is proportional to the density of the absorbing material, we can calculate the values of β from the values given by Sadler * for their coefficient in air.

Sadler † has measured the coefficients of absorption in air of the fluorescent radiations characteristic of copper and arsenic, and he and Barkla ‡ have shown that the ratio of the coefficients of any two fluorescent beams is constant for all absorbing substances in which these beams do not excite a fluorescent radiation. We can, therefore, calculate the values of λ_2 in air from those in aluminium and in air given by Barkla and Sadler.

The fluorescent rays used were those from chromium, iron, zinc, and tin, and with the exception of tin Barkla and Sadler § have measured their absorption coefficients in gold and silver. Their value for the coefficient of the rays from chromium in gold is unreliable according to their statement, but it will be seen that λ_1 is always so small with respect to β that an exact knowledge of this quantity is not important.

The absorption coefficients of the rays from tin in gold and silver are not given by the above writers, but may be obtained approximately from the constant ratio between absorption coefficients cited above. Tin rays, being more penetrating than those characteristic of silver and gold, will excite their fluorescent radiations and, therefore, will probably be less penetrating to these metals than the above calculation would indicate, but an inspection of the curves given by Barkla will show that the increase of absorption is not very great in this part of the spectrum, and it will be seen that the effect of λ_1 is negligible in the case of the rays from tin.

The accompanying tables give the values of the quantities occurring in the formula as calculated from the data given by Barkla and Sadler and the observed values of *e/i* in gold and silver. The last column gives the values of R as calculated from these results. Most of the values of *e/i* were obtained using only one sheet of metal foil, but in some cases more than one sheet was used. As the terms in the formula containing t drop out when t is equal to or greater than two sheets of the metal, and as no consistent variation with the thickness of the sheets was observed, the mean of *all* the values of e/i using more than one sheet and the resulting values of R are given separately in the tables following the greater value of t.

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* Phil. Mag. vol. xxii. p. 447 (1911).

† *Loc. cit.*

‡ Phil. Mag. vol. xvii. p. 739 (1909).

§ *Loc. cit.*

Gold.

Radiator λ_1 in Al.	λ_1.	λ_2.	$\beta \times 10^{-4}$.	$t \times 10^5$ cm.	S.	$\epsilon^{\lambda_2 t'}$.	$S\epsilon^{\lambda_2 t'}$.	e/i Obs.	R.
Chromium 367	9780	0·0321	70·0	0·8	1·03	1·07	1·10	1·30	1·18
				$\geqq$ 1·6	1·03		1·10	1·34	1·22
Iron 239	7070	0·0209	66·0	0·8	1·01	1·05	1·06	1·31	1·24
				$\geqq$ 1·6	1·02		1·07		
Zinc 106·3	3438	0·0093	57·5	0·8	1·01	1·01	1·02	1·21	1·19
				$\geqq$ 1·6	1·01		1·02	1·25	1·23
Tin 4·33	106·4	0·0004	10·7	0·8	1·00	1·00	1·00	1·15	1·15
				$\geqq$ 1·6	1·00		1·00	1·16	1·16
Silver.									
Chromium 367	6095	0·0321	38·0	1·8	1·02	1·07	1·09	1·33	1·22
				$\geqq$ 3·6	1·03		1·10	1·40	1·27
Iron 239	4000	0·0209	35·8	1·8	1·03	1·05	1·08	1·31	1·21
				$\geqq$ 3·6	1·02		1·07		
Zinc 106·3	1830	0·0093	31·4	1·8	1·02	1·01	1·03	1·24	1·20
				$\geqq$ 3·6	1·01		1·02		
Tin 4·33	23·02	0·0004	5·75	1·8	1·00	1·00	1·00	1·23	1·23
				$\geqq$ 3·6	1·00		1·00	1·23	1·23

It is at once apparent from the tables that the ratio of emergence to incidence cathode rays does not vary with the penetrating power of the exciting X-rays in the range of penetrating powers used; that is, for an increase of absorbability as measured in aluminium of about 8000 per cent. there is no measurable variation in the ratio.

It is interesting to note in this connexion the values of the ratio compared with those found by Stuhlmann for the cathode rays produced by ultra-violet light. The value he gives for silver is 1·07, and for platinum, which seems to behave, for X-rays at least, about the same as gold, 1·17. This is about the same as the mean of all the values which I have obtained for gold. His value for silver is somewhat less than the mean of my determinations. If the mechanism of production of cathode rays is the same with ultra-violet light as it is with X-rays, the ratio of emergence to incidence effect does not seem to vary much over a range of absorbability corresponding to the X-rays from tin up to that corresponding to ultra-violet light.

Summary.

The ratio of emergence to incidence cathode rays produced in gold and silver by beams of fluorescent secondary X-rays has been measured with the object of finding the dependence of the ratio on the penetrating power of the exciting rays.

The fluorescent secondary X-rays from tin, zinc, iron, and chromium were used as exciting rays, representing an increase in absorbability as measured in aluminium of about 8000 per cent. between tin and chromium.

After allowing for the absorption of the exciting rays in the layer of the metal from which the cathode rays come and in the air of the ionization-chamber it was found that there was no definite variation in the ratio of emergence to incidence effect.

In closing I wish to express my thanks to Professor H. A. Bumstead for the interest he has taken in the work.

Sheffield Scientific School,
Yale University, New Haven, Conn.
March 1912.

IV. *On the Thermal Conductivity of some Rocks at High Temperatures.* *By* Horace H. Poole, *M.A.*, *Sc.B.*[*]

A KNOWLEDGE of the thermal conductivity of rocks at high temperatures being of considerable importance in some geophysical problems, an attempt has been made to ascertain how the conductivity varies as the temperature is raised in the case of some typical rocks. The method employed is the well-known one of generating heat electrically at a known rate uniformly along the axis of a long cylinder of rock, and measuring the difference of temperature between two points at different distances from the axis.

[*] Communicated by the Author.

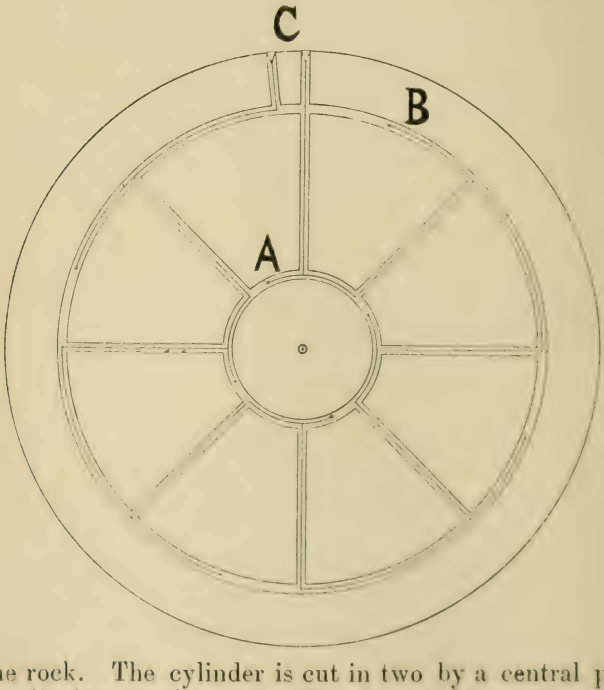
Then if Q calories be generated per second per centimetre length along the axis and Δ be the difference of temperature between two points distant r_1 cm. and r_2 cm. respectively from the axis, we have

$$K = \frac{Q}{2\pi\Delta} \log_e \frac{r_2}{r_1},$$

where K is the thermal conductivity. This equation of course only holds for points sufficiently remote from the ends of the cylinder and for steady temperatures.

The rock is placed in a tube electric furnace maintained at a constant temperature; along the axis of the cylinder a hole is drilled through which runs a platinum wire by means of which heat can be electrically generated at a known rate. The temperatures are measured by means of platinum, platinum-iridium thermo-couples. As the boring of fine holes especially in the harder rocks is exceedingly difficult, some other method has to be adopted for sinking the couples in the rock. The cylinder is cut in two by a central plane perpendicular to the axis. The two halves are ground together with fine carborundum powder until an accurate fit is attained. A system of fine grooves as shown in fig. 1,

Fig. 1.



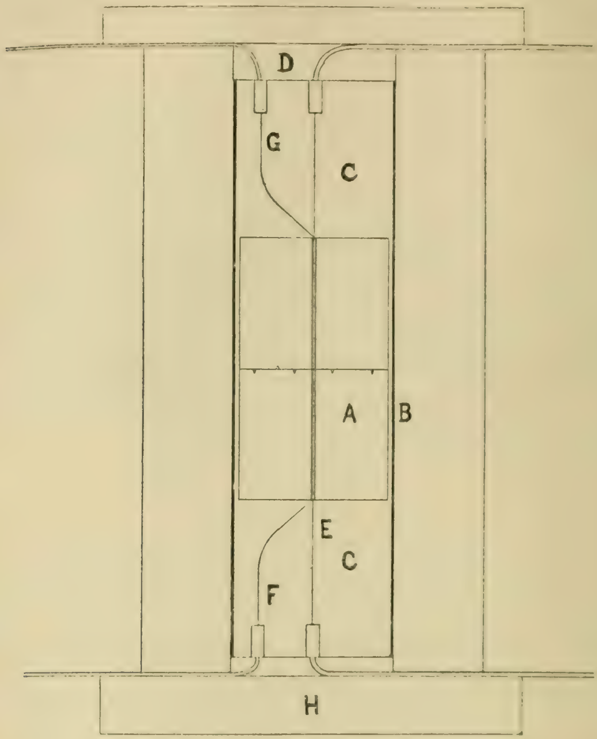
which represents a limestone cylinder, is then cut in one face, and a multiple couple with four pairs of junctions is sunk in them, one set of junctions being equally spaced round the circumference of the inner circular groove and the other set round the outer circle. In the figure, A is one of the inner junctions and B one of the outer. The grooves are V-shaped, the couple being sunk to the bottom of the V and the groove filled in with some kind of cement. The junctions are situated in the circular grooves at points approximately midway between the radial grooves so as to minimise errors due to the latter. The free ends of the couple are cemented into grooves C cut in the outer surface of the cylinder parallel to the axis. This couple measures the average differences of temperature between points on the inner and outer circles whose radii are known. The average temperature of the rock is measured by a single couple cemented into a straight groove cut in the ground face of the other half of the cylinder, so that the junction is at a known distance from the centre. The two halves are then carefully cemented together, the layer of cement between the two faces being as thin as possible.

Limestone.

The first determination was made on limestone, it being an easy rock to work, and the results obtained for it being of less importance than those for the igneous rocks. The total length of the complete cylinder is 13·67 cm. and the diameter 7·89 cm., the diameters of the circular grooves being 1·94 cm. and 6·36 cm. respectively. The distance of the single couple from the axis is 1·93 cm. The grooves are V-shaped, about 2·5 mm. deep, and 1 mm. wide at the top. The wires of the couple are 0·1 mm. in diameter, the junctions being twisted together and fused in a Meker burner. The cement used with the limestone and also with the granite is a mixture of very finely powdered fireclay with water-glass. This cement, though satisfactory when set, is very difficult to work, and great difficulty was experienced in cementing in the fine wires with it, so that in some experiments at present being carried out on basalt, other cements have been tried. The central hole is about 1·5 mm. in diameter and the platinum wire 0·3 mm. diameter, the space round the wire being filled with fine carborundum powder. This material was not a very happy choice, as it is liable to attack platinum at high temperatures, but in this case no harm was experienced with it.

The arrangement of the rock and furnace is shown in section in fig. 2. A is the rock cylinder. The circular grooves carrying the multiple couple for measuring the temperature difference are shown in section, also the single groove carrying the single couple. B is a copper tube 30·5 cm. long, 8·3 cm. internal diameter, and about 1·6 mm. thick. The annular space between A and B is filled with fine carborundum powder. The object of using a copper tube is to ensure that the whole furnace shall attain as uniform a temperature as possible. To lessen oxidation at high temperature the tube was coated both inside and outside with blacklead. The furnace winding (not shown in the figure) is of nickel wire 2 mm. diameter uniformly wound in a single layer on the copper cylinder, but insulated from it by asbestos millboard. The successive turns of bare nickel wire are prevented from touching by a thin wire with a thick asbestos insulation. This thin wire carries no current, and might be replaced by asbestos cord.

Fig. 2.



To lessen oxidation of the furnace winding it was thickly coated with fireclay cement, and while the latter was still liquid several successive layers of asbestos millboard were bound round the whole as tightly as possible. Outside this is a lagging of asbestos-wool enclosed in a cylinder of several sheets of asbestos millboard. The sketch indicates approximately the total thickness of the lagging. The winding is put on in two separate equal circuits, the turns of one lying between those of the other. The circuits may be connected either in series or parallel to facilitate the current regulation. As the energy to be supplied to the furnace varies widely according to the temperature required, this arrangement is very convenient. The spaces C at either end of the rock cylinder are filled with asbestos disks with small holes bored in them to carry the necessary wires, the spaces D outside the end of the copper tube are filled with asbestos-wool. The heating-wire E runs almost the entire length of the furnace and is connected by bind-screws to stout leads as shown. Two other platinum wires F and G are attached to D at the ends of the cylinder and are used for measuring the potential difference between these points. The furnace stands on a thick pad of asbestos millboard H, and a similar one is laid over the top, care being taken to exclude the circulation of air as far as possible. The wires leading to the couples are not shown in the figure; a pair of platinum wires leading to the multiple couple enter at the bottom of the cylinder, and a pair of wires, one platinum and the other platinum-iridium, forming the single couple enter at the top.

The current which flows through E is supplied by a large storage-battery and regulated by a rheostat. It is measured on a Kelvin portable combined ammeter and voltmeter, the potential difference between F and G being read on the same instrument. In this way the rate of generation of heat in the known length of the heating-wire inside the rock cylinder is found.

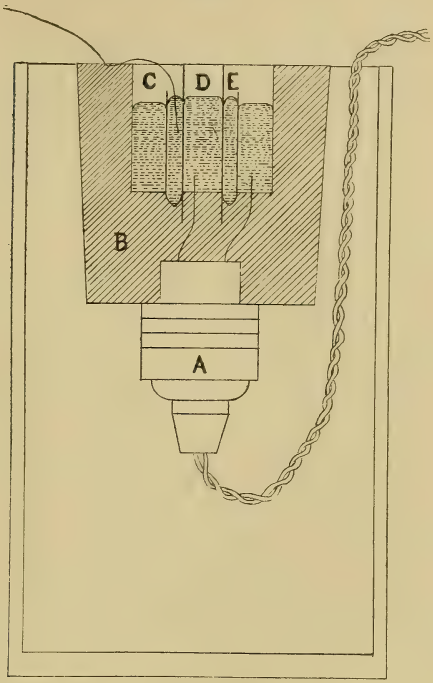
The furnace current is alternating, being obtained from the Dublin City Supply. For all the limestone determinations and most of those for granite, the current was transformed down to 10 volts and the two furnace circuits connected in parallel. In the highest temperature determinations with granite, the circuits were connected in series and current at 40 volts employed.

There are several advantages in using low voltage alternating current for the furnace, the chief being that by so doing insulation troubles are greatly lessened, and the danger of errors being introduced into the readings of the very small P.D.'s of the couples by leakage from the furnace circuit is almost entirely obviated. The possibility of a leak from the central wire causing an error was tested, and it was found that switching off the current through the central wire produced no effect on the readings of the couples until sufficient time had elapsed for the temperature change to reach the couple, so that evidently no leakage of current occurred.

The current through the furnace is entirely controlled by means of a choking-coil, consisting of a solenoid containing about 250 turns of insulated copper wire 3 mm. in diameter wound on a glass tube 30 cm. long by 2·2 cm. internal diameter. In this fits a bundle of varnished soft-iron wires furnished at one end with a pointer moving over a scale, so that the position of the core can be noted. By moving the core into the coil the current is reduced, and *vice versa*. By this means an exceedingly long range of continuous control is obtained, and as comparatively little energy is wasted in the choking-coil, it does not overheat seriously. When the furnace is being heated up in the morning the choking-coil may be short-circuited by means of a suitable switch. A Siemens dynamometer was converted into a wattmeter by making new windings, and used to measure the energy supplied to the furnace. As the instrument was only roughly calibrated its readings are only relative, but are useful in adjusting the supply of energy to the furnace so as to obtain a constant temperature as quickly as possible.

The wires leading from the couples are connected to a mercury switch so that either couple may be connected to the potentiometer. This switch, which is designed to eliminate irregular thermal effects and somewhat resembles one for a similar purpose described by Lees, is illustrated, partly in section, in fig. 3. A is an ordinary bayonet lamp-holder connected to electric light twin flex in the ordinary way except that in addition to the copper conductors a stout platinum wire is fixed in each screw-contact. On the lamp-holder are screwed as many shade-holder rings as will fit to increase the mass of metal surrounding the platinum-copper contacts enclosed, and so ensure their equality of temperature. The open end of the bayonet-holder is imbedded in a slightly tapered cylinder of paraffin-wax B in the top of which is a cylindrical cavity C. In the centre of this is fixed a thin glass tube D round which are fixed ten quill glass tubes E. The platinum wires leading from the bayonet-holder, and so from the potentiometer, lead into the central tube D and the annular space C respectively, as shown in the figure. The tubes and space C contain pure mercury, and

Fig. 3.



each couple wire is led into a separate one of the small tubes, from which, by means of small pieces of platinum wire, connexion may be made to the inner and outer compartments. The couple wires are fixed to the key by warming the top of the paraffin-wax with a hot glass rod and pressing the fine wire down into the molten wax as shown. The whole key is placed in a glass vessel, shown in section in the figure, and the intervening space filled with cotton-wool. It will be seen that in this key the various contacts are all surrounded by a large mass of metal, which in turn is jacketed by a layer of material of low thermal conductivity, so that the temperature of the mercury and also of the lamp-holder surrounding the lower junctions must be very nearly uniform throughout, even when the key is comparatively near the furnace as it must necessarily be. Only platinum and platinum-iridium wires come into contact with the mercury which does not amalgamate with them. Only four out of the ten small tubes are employed; but this is no disadvantage, and the key could if necessary be used for five couples. As the key in effect forms the cold junction of the single couple, a knowledge of its temperature is necessary, and is obtained by means of a thermometer placed in C. This key has always proved very satisfactory, and no irregularities have ever been traced to it. The other end of the flex leading from the key is connected direct to the potentiometer, in using which due care is taken to minimise thermal effects at bind-screws and contacts as far as possible. The galvanometer employed was an Ayrton and Mather giving a deflexion of about 17 scale-divisions per microvolt, but this instrument was inconveniently sensitive.

In the earlier experiments a sufficiently sensitive potentiometer not being available, the E.M.F.s of the couples were measured by balancing them against the P.D. across the ends of a known resistance, either one ohm or ten ohms, through which a known very small current flowed. The current was calculated from the known voltage of the dry cell driving it and the resistance of the circuit, which was always so large that the resistance of the cell might be neglected. The resistance of the circuit was varied until a balance was attained. The voltage of the cell was measured daily by means of a Crompton potentiometer, and only varied by about 0·2 per cent. during the whole period of use.

Shortly after the work was started a Tinsley potentiometer was obtained reading to microvolts, and this was always used subsequently.

In heating up the furnace in the morning the choking-coil is short-circuited until the required temperature is attained. The supply of energy to the furnace is then adjusted by trial until as steady a temperature as possible is attained. In the case of the higher temperatures this could not be done until the evening. Considerable trouble was experienced owing to the variation in voltage of the city supply. A self-regulating arrangement for overcoming this difficulty will be described in a later paper. In the case of the determinations at temperatures below 100° C. no current was passed through the furnace when a steady state had been reached. The lowest temperatures could only be attained by reducing the supply of energy from the central wire. An approximate correction for small temperature changes can be made as follows. Denoting for the future θ as the average temperature of the rock indicated by the single couple, and Δ as the temperature difference indicated by the multiple couple, it is always found that when an approximately steady state is reached $\frac{d\Delta}{dt}$ is very small compared with $\frac{d\theta}{dt}$; so we may assume that the rate of change of temperature of every part of the rock is approximately $\frac{d\theta}{dt}$. So if Q calories be generated per second per centimetre along the axis and C be the thermal capacity of the rock per unit volume, we have for a distance ρ from the axis

$$-2\pi\rho K\frac{d\theta}{d\rho}=Q-\pi\rho^2c\,.\,\frac{d\theta}{dt}\;;$$

$$\therefore\quad -\frac{d\theta}{d\rho}=\frac{Q}{2\pi K\rho}-\frac{c\rho}{2K}\cdot\frac{d\theta}{dt}.$$

So

$$\Delta=\frac{Q}{2\pi K}\log_e\frac{r_2}{r_1}-\frac{c(r_2^2-r_1^2)}{4K}\cdot\frac{d\theta}{dt}.$$

Now for the limestone cylinder,

$$r_1=0{\cdot}97\text{ cm.}$$
$$r_2=3{\cdot}18\text{ cm.}$$
$$c=0{\cdot}53\text{ about.}$$

If A be the current in amperes flowing through the central wire and V be the P.D. in volts across the ends of the cylinder, $W=AV$ is the energy liberated in watts inside the cylinder, and $Q=\frac{W}{13{\cdot}67\times 4{\cdot}18}$, since the cylinder is 13·67 cm. long. Putting in these figures we obtain

$$K=\frac{3{\cdot}304W-20{\cdot}3\alpha}{\Delta}\times 10^{-3},$$

where α = the rate of rise of average temperature in degrees per minute. We may write this equation

$$K=3{\cdot}304\times\frac{W'}{\Delta}\times 10^{-3},$$

where $W'=W-6{\cdot}15\alpha$, and may be regarded as the effective watts. In applying this correction two sets of readings of W, θ, and Δ are taken, and the mean values of W and Δ taken and used in the above equation. The value found in this way generally only differs slightly from what would be obtained by neglecting α.

The thermoelectric properties of the wires used for the couples were tested at the National Physical Laboratory, and from the figures thence obtained a curve was carefully plotted showing the E.M.F. of a single couple whose cold junction is at 0° C. and whose hot one is at θ° C. As in practice the cold junction temperature is that of the key θ_1, an easily calculated correction has to be added to the observed E.M.F. E_1 to obtain the value of the E.M.F. E_2 corresponding to a cold junction at zero, from which the temperature θ may be read off to the nearest degree on reference to the curve. If the distance of the single junction from the centre were the geometric mean of the distances of the inner and outer junctions of the multiple couple, the temperature of the single junction would be the mean of the temperatures of the other junctions. This condition is sufficiently nearly realized. A second curve is plotted showing the thermoelectric power at various temperatures. From this, knowing the mean temperature of the junctions of the multiple couple we obtain the difference of temperature Δ indicated by a given E.M.F. E_3.

In obtaining α the total change of temperature is often very small, so the increase in E_2 is divided by the thermoelectric power for the given temperature and by the time in minutes between the two sets of observations. The time was always read at the moment of reading E_1.

The following table (No. I.) gives a typical day's work. The first column gives the time, the second the position of the indicator on the core of the choking-coil, and the third the reading of the wattmeter measuring the energy supplied to the furnace. The power in watts is about four times the reading of the wattmeter. The other columns show the values of quantities already mentioned; under K is found the conductivity deduced from a single set of readings, while under K′ is that obtained from a pair of sets correcting for temperature change. In certain cases where several hours have elapsed between successive readings and where the temperature change in that time is small, the value obtained for K from the last single set of readings may be nearer the truth than the value K′, as towards the end the temperature change must be very slow except for irregular changes due to voltage variation. For this reason in adopting a mean result for K for a day's work, due regard is paid to the figures in both columns K and K′.

TABLE I.

The furnace and central wire currents were turned on at 10.9 A.M., the choking-coil being short-circuited. The furnace current was turned off at 10.41 A.M., and turned on again at 12.5 P.M., the coil being in circuit, the core was altered to 20·0 at 1·32 P.M.

			A.	V.	W.	E_1.	θ_1.	E_2.	θ.	$100a$.	W′.	E_3.	Δ.	$K\times10^3$	$K'\times10^3$
A.M. 11.45	...	...	5·15	3·19	...	1559	16·2	1747	143	...	...	803			
P.M. 12.5	20·7	13·5	5·14	3·18	...	1528	16·4	1719	141	...	...	787			
1.10	,,	15·5	5·12	3·18	...	1588	17·1	1787	146	...	...	711			
1.32	20·0	12·5	5·11	3·18	...	1620	17·4	1822	149	...	...	704			
2.13	,,	13·5	5·09	3·17	...	1650	17·7	1856	152	...	...	727			
3.25	,,	12	5·08	3·17	16·10	1702	17·7	1908	156	...	...	751	14·18	3·75	
										1·68	15·96				3·74
3.52	,,	12	5·07	3·16	16·02	1700	18·4	1914	156		...	743	14·02	3·77	
										3·11	15·82				3·72
4.55	,,	13	5·06	3·16	15·99	1723	18·6	1940	158	...	...	751	14·12	3·74	

E.M.F.s of couples are expressed in microvolts and all temperatures in degrees centigrade. The mean result taken from this day's work is $K=3{\cdot}73\times10^{-3}$ at a temperature of 157° C. It is evident that the figures in the first column are all too large as the temperature was rising continuously.

Table II. gives the results obtained for limestone arranged

TABLE II.

θ.	$K\times10^3$.	W.	θ.	$K\times10^3$.	W.	θ.	$K\times10^3$.	W.
91	4·92	12·60	160	4·08	16·13	72	3·96	8·59
72	5·25	9·82	302	3·68	16·27	243	3·32	16·54
59	5·40	7·55	320	3·66	16·21	276	3·25	16·48
35	5·68	3·56	186	3·93	15·19	227	3·40	16·29
239	4·10	13·75	370	3·31	15·00	195	3·47	15·76
297	3·99	14·13	135	3·72	15·92	135	3·675	15·58
266	4·11	5·55	92	4·06	13·46	114	3·80	15·12
361	3·45	8·47	40	4·56	4·66	60	4·30	6·94
326	3·655	9·65	317	3·23	10·00	125	3·86	15·79
388	3·47	11·42	157	3·73	16·04	352	3·20	15·53
286	3·61	5·73	77	4·23	9·44	366	3·17	16·63
238	3·83	14·83	315	3·28	16·42			

in chronological order. The value of W is also given, as it is possible that an apparent variation of K with W might occur. No such effect is noticeable in the case of the limestone. The results are plotted in fig. 4, and it is at once apparent that they may be divided into three series. The first 7 results lie fairly well along the upper curve, whose equation is

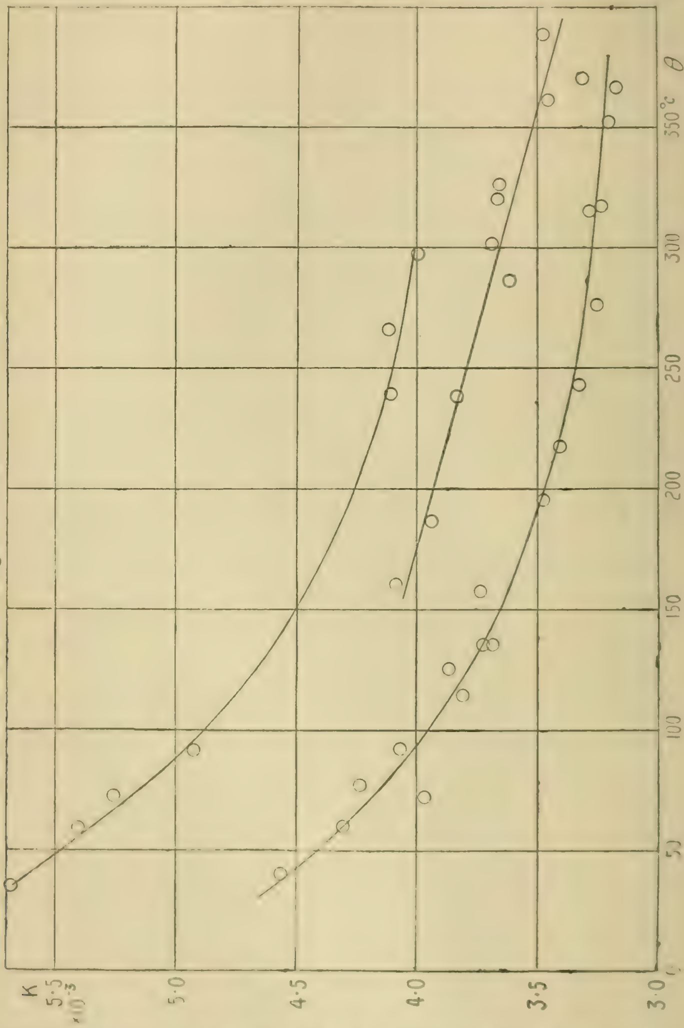


Fig. 4.—Limestone.

$$K=(3{\cdot}835+2{\cdot}59\,e^{-0{\cdot}00914\,\theta})\times 10^{-3},$$

or when written in the most convenient form for calculation

$$\log [K-0{\cdot}003835] = \bar{3}{\cdot}4130 - 0{\cdot}00397\,\theta.$$

The next 9 results, beginning with that for a temperature of 361°, lie roughly along a right line

$$K = [4{\cdot}48 - 0{\cdot}00275\,\theta] \times 10^{-3}$$

between the limits of temperature 160° and 390°.

The last 19 results, beginning with that for a temperature of 370° C., which, however, seems to be of a somewhat transitional nature, lie approximately along the lower curve

$$K = (3{\cdot}14 + 1{\cdot}99\,e^{-0{\cdot}00914\,\theta}) \times 10^{-3},$$

$$\text{or} \qquad \log (K - 0{\cdot}00314) = \bar{3}{\cdot}2989 - 0{\cdot}00397\,\theta.$$

It will be noticed that the coefficient of θ is the same in the first and last curves.

The progressive lowering of the conductivity is due to baking of the stone, which was found to be greatly altered when it was finally removed from the furnace. The first member of the second and also that of the third series are high temperature determinations, which probably caused permanent alteration in the rock, though in the case of the third series a higher temperature than 370° had previously been attained. The fact that so many results lie approximately on the curve seems to indicate that the condition of the rock had become approximately constant. The first and third series are the most interesting, showing respectively the fall in conductivity when the rock is first heated and the variation of conductivity with temperature when the rock has been several times raised to over 350° C. The transitional results in the second series seem to be less interesting.

Slate.

An attempted determination on slate failed as the rock split when heated.

Granite.

The arrangement adopted with granite is identical with that used with limestone. The cylinder of medium-grained Mourne granite is 13·90 cm. long and 7·86 cm. in diameter. The diameters of the inner and outer grooves are 1·833 cm. and 6·156 cm. respectively. The specific heat and density of granite being about the same as that of limestone, we have, putting in these figures,

$$K = 3 \cdot 319 \times \frac{W'}{\Delta} \times 10^{-3},$$

where $$W' = W - 5 \cdot 78\,\alpha,$$

the various letters having the same meaning as before. A typical determination is shown in Table III., the various columns having the same signification as before.

TABLE III.

The furnace current was turned on at 10.31 A.M., the choking-coil being short-circuited. The choking-coil was first put in circuit at 12.54 P.M. The central wire current was turned on at 11.21 A.M.

			A.	V.	W.	E_1.	θ_1.	E_2.	θ.	$100a$.	W'.	E_3.	Δ.	$K\times10$	$K'\times10^3$
P.M. 12.52	...	112	...	...	...	4309	15·4	4488	336						
12.54	30·0	62	4·59	3·00	13·77	...	...	...	...	...	...	268			
1.16	„	58	4·59	3·00	13·77	4479	16·0	4665	347	...	...	629			
										−4·37	14·02				
2.16	„	—	4·59	3·00	13·77	4429	16·9	4625	345	...	...	666	10·91	4·19	
										−2·37	13·89				4·23
2.52	„	56	4·58	3·00	13·74	4411	17·3	4612	344	...	...	664	10·88	4·185	
										0	13·74				4·21
3.45	„	60	4·58	3·00	13·74	4407	17·6	4612	344	...	...	657	10·77	4·23	
										0·88	13·69				4·24
4.52	„	59	4·58	3·00	13·74	4413	17·9	4621	345	...	...	650	10·65	4·28	
										0·16	13·73				4·245
5.34	„	58	4·58	3·00	13·74	4413	18·0	4622	345	...	...	661	10·82	4·215	

Mean value $K = 4 \cdot 23 \times 10^{-3}$ at 345° C.

A peculiarity noticed with the granite which had not appeared with the limestone, is the apparent rise in the value of K with decrease in W. It was found that this is partially, at least, explained by the fact that a small temperature difference is indicated by the multiple couple when the furnace is heated and the temperature steady, no energy being generated in the central wire. Under these circumstances the axis of the cylinder is at a slightly lower temperature than the outer parts, so that when only a small quantity of heat is evolved in the central wire, the observed value of Δ is too low, and so the apparent value of K is too high. With larger values of W this error becomes unimportant. It was thought that this central cooling might be due to vertical circulation of air leaking through the asbestos, so in the later determinations the furnace was laid horizontally, but this did not cause any improvement. The only way of eliminating this error is by the use of a longer or narrower furnace and cylinder. However, by using comparatively large values of W, and hence of Δ, the error becomes negligible and consistent results are obtained.

The results obtained for granite are shown in Table IV.

TABLE IV.

θ.	$K \times 10^3$.	W.	θ.	$K \times 10^3$.	W.
200	4·73	8·31	[315	4·55	6·36]
88	5·04	6·85	[292	5·32	2·95]
75	5·17	6·38	345	4·23	13·72
385	4·27	13·06	450	4·22	25·52
203	4·30	11·42	537	3·95	25·19
84	4·61	6·98	443	3·95	10·51
288	4·25	15·35			

The results in brackets, which were both obtained on the same day, are disregarded, the values for K being too large owing to the small values of W, and the high temperature of the furnace as explained above. The other results are plotted in fig. 5. As in the case of the limestone, progressive lowering of the conductivity occurred though to a less extent.

The first three results lie on a curve somewhat similar to those obtained with the limestone.

The next six, beginning with that for a temperature of 385°, lie along the curve

$$K = (4{\cdot}215 + 1{\cdot}07\, e^{-0{\cdot}01187\,\theta}) \times 10^{-3},$$

or $$\log (K - 0{\cdot}004215) = \bar{3}{\cdot}0296 - 0{\cdot}005155\,\theta,$$

the first member being slightly above the curve.

The last two determinations at 537° C. and 443° C. gave the same result $K = 3{\cdot}95 \times 10^{-3}$, indicating further lowering of the conductivity when the rock was heated above 450°.

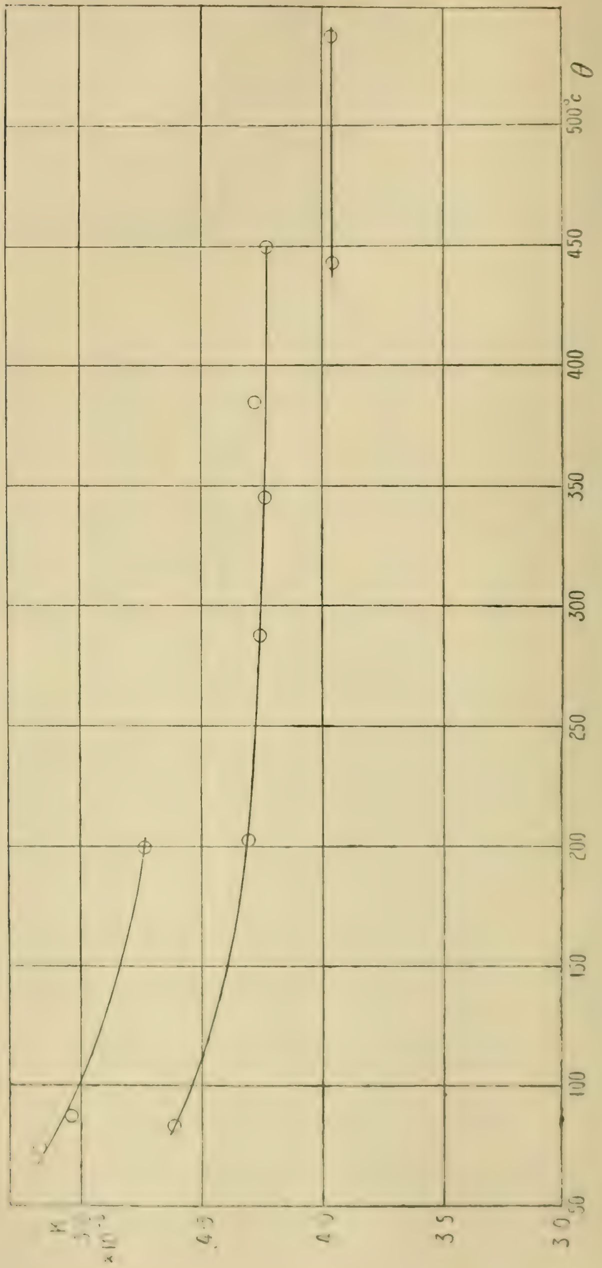


Fig. 5.—Granite.

The experiment was unfortunately brought to an untimely conclusion by the breaking of the multiple-couple inside the furnace during an attempt to obtain the value of K at 650° C. The rock on removal from the furnace was found to have been considerably altered, being much whiter and less hard than before. The change is probably due to the formation of very minute cracks which would explain the permanent lowering of the conductivity.

Sources of Error.

The chief errors likely to affect the results are those due to end effects, which are very difficult to allow for. These errors seem likely to occur in three ways, though their effects are probably small when the conditions of the experiment are suitable.

As already stated, when the furnace is heated and no heat is generated in the central wire, the axial temperature is, in the case of the granite at least, slightly lower than that of the outer parts of the rock. If only a small quantity of heat is generated in the central wire, this error will make Δ too small and K apparently too large. This error will increase with increase in θ and with decrease in W.

On the other hand, the ends of the furnace are filled with asbestos, which is certainly a worse conductor than the rock, so that the radial temperature gradient due to the central wire will be much greater in it than in the rock, *i. e.* when a large amount of heat is developed in the central wire the axial temperature at the ends of the rock cylinder will be too high. That the axial temperature is actually higher in the asbestos ends than in the rock for large central wire currents is shown by the fact that on one occasion the central wire fused in the asbestos when the mean temperature of the part in the rock was far below the melting-point of platinum, as obtained from the readings of the ammeter and voltmeter just before the fusing occurred. This high axial temperature at the ends of the rock cylinder affects the apparent value of K in two opposite ways. Firstly, by conduction along the axis the centre radial temperature gradient is made too large, and consequently K too small. Secondly, as the axial temperature is higher near the ends the resistance per centimetre of the central wire, and consequently the heat evolution per centimetre, is greater near the ends than in the middle, so that the rate of evolution of heat per centimetre in the middle, where the gradient is measured, is less than the average for the whole length of wire in the rock cylinder. As it is the latter value that is used in calculating K, this error tends to make the value of K found too large.

It is evident that these errors will be greatly influenced by the rate of heat evolution in the central wire. As in the case of the limestone, no regular change in K is noticeable with change in W, and the same holds good for granite except when $\theta > 250°$ and $W < 8$: it would seem as if the errors are not very important. It must be remembered that the ratio of the length of the cylinder to its radius compares very favourably with the ratio of the diameter to the thickness of the plate used in many guard-ring determinations.

In experiments at present being conducted on basalt, the dimensions of the furnace have been so modified as to greatly reduce all these possible errors. It is hoped to repeat the determination for granite with this furnace and new cylinders of rock.

It has recently been found that thermal effects at the potentiometer may introduce small errors, but these generally only amount to a few microvolts, so that their effects would not be of much importance, especially in those determinations in which W and hence Δ are large.

The permanent lowering of the conductivity when the rock is heated under atmospheric pressure unfortunately detracts considerably from the value of the results from a geophysical standpoint, as the conductivity of heated rocks beneath the earth's crust may be considerably greater than the figures given above. On the other hand, the conductivity of the deep-seated rock is almost certainly less than the value obtained at first for the unaltered rock at temperatures below 100° C., so in the case of granite similar to the specimen used it would seem probable that for temperatures up to 450° the conductivity must be between 0·0042 and 0·0050.

In conclusion I wish to express my gratitude to Dr. Joly, at whose suggestion the work was carried out, for his kind interest and many valuable suggestions during its progress.

Physical Laboratory,
Trinity College, Dublin,
April 29, 1912.

V. *Breaking Tests under Hydrostatic Pressure and Conditions of Rupture.* *By* P. W. Bridgman[*].

[Plate II.]

WITHIN the last few years a number of papers[†] have appeared, either written by engineers or else of engineering interest, dealing with the conditions under which rupture is produced in the materials of ordinary practice. The objects of these papers has been to find if possible some criterion by which rupture may be predicted, whatever the type of applied stress. The present state of opinion seems to be that for ductile materials the maximum shearing stress plays the principal part, but that for brittle materials the maximum principal stress is the determining factor. At the same time it is pretty generally recognized that neither of these criteria is likely to be actually correct, but is at best only an approximation likely to give fairly good results for the materials of ordinary engineering practice under ordinary practical systems of load.

A general consideration of what may be the determining factors in producing rupture under so wide a variation in the nature of the applied stress that there is no immediate relation to the needs of engineering seems to have been neglected. Yet it is precisely such a consideration of the conditions of rupture under as wide a range of the conditions as possible that is likely to lead to a true theory of rupture, and so to a better formulation of the conditions for the range of ordinary practice.

In the course of a number of experiments on very high hydrostatic pressures, the author has observed many cases of rupture which have a bearing on the present question. The pressures which it has been found possible to reach are considerably in excess of any hitherto produced in fluids, pressures of 30,000 atmos. having been repeatedly attained. Under these pressures all ordinary theories as to the behaviour of elastic solids break down completely, and the entire subject had to be approached from the beginning. During the two or three years of preliminary work spent in acquiring familiarity with the methods by which these pressures might be handled, many cases of rupture have been observed. Several of these appear to be of types not observed before, and they have special bearing on the present question. In this paper three of these types of rupture will be described somewhat in detail, and a discussion given of the bearing of these tests on theories of rupture. No attempt will be made to develop a new theory. All that it is desired to do is to point out that in consequence of these tests the true criterion of rupture must be a much more complicated affair than is ordinarily supposed, and that considerations must be introduced which have been so far neglected, for these tests enable us to summarily dismiss all the conditions of rupture hitherto proposed

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[*] Communicated by the Author

[†] Scoble, Phil. Mag. xii. pp. 533–547 (1906); Hancock, Phil. Mag. xii. pp. 418–425, 426–430 (1906), and xvi. pp. 720–725 (1908); Gulliver, Proc. Roy. Soc. Edin. xxix. pp. 427–431 (1909); Smith, Eng. lxxxviii. pp. 238–243 (1909); Scoble, Phys. Soc. Lond., Nov. 26, 1909; xxii. pp. 130–146 (1910).

The tests to be described in this paper fall naturally into three types, and the conditions of rupture to which they have application are also three in number, there being one other generally recognized possibility besides the two mentioned in the first paragraph. Each of the three types of tests gives some evidence on the validity of each of the three conditions of rupture, but it will be found that each of the three types of test has its most direct bearing on only one of the conditions. The argument of the paper is grouped about the three different types of test. The nature of the test is first described, then the bearing on the corresponding condition of rupture, and finally the incidental bearing on the other conditions of rupture. The argument is furthermore somewhat complicated by the necessity for keeping in mind the possibility of different criteria holding for brittle and ductile bodies.

The three conditions of rupture to be considered are the condition of maximum principal stress, of maximum stress difference, and of maximum strain. The first demands that rupture occur when either principal stress exceeds a certain value, whether this stress is compressive or tensile. The second demands that failure occur when the greatest shearing stress, or what is the same thing the difference between the greatest and the least principal stress, exceeds a certain value. The third criterion demands that rupture occur if the extension in any direction exceeds a critical value.

Another question of much practical interest, and under ordinary conditions closely related to the question of rupture, is the question as to the conditions under which a material will receive a permanent set. The three criteria just enumerated are very often used interchangeably as either criteria of rupture or as criteria of set.

The first criterion, as originally stated, evidently cannot hold without modification, for it demands that a solid body when subjected to uniform hydrostatic pressure all over should break when the pressure rises too high. It is inconceivable in this case how the body can break, and the existence of the heavenly bodies with enormous internal pressures is conclusive proof to the contrary. It is still possible, however, that this criterion should be valid as determining set, and that the body might show volume set if the pressure exceeded a certain critical value. This is a question of some interest, and it might possibly seem reasonable at first sight to expect some such set. Kahlbaum * has published results on this subject showing the very surprising result that after the application of pressures up to 10,000 atmos. the density of most metals is increased, due to closing up of small pores, but that beyond 10,000 the density is decreased. Although no systematic investigation of this question has been made in the present work, several incidental determinations have been made up to 25,000 or 30,000 atmos., and no trace of a change of density has ever been found except in those cases where the metal was obviously porous. There seems to be no question but that Kahlbaum's results were due to the fact that he used castor oil to transmit pressure. This freezes under a few thousand atmos., a fact that Kahlbaum overlooked, so that beyond this, his pressure was no longer hydrostatic. This is shown most strikingly by Kahlbaum's own statement that the test cubes were often curiously distorted after application of pressure. Kahlbaum saw in this support of his theory that all metals tend to become plastic or even fluid under high hydrostatic pressures. But it can be stated unqualifiedly from the present work that, on the contrary, substances tend to become more rigid under high pressures. The distortion of the metal cubes found by Kahlbaum is to be explained by the fact that the effect of pressure in increasing rigidity is very different for different substances. It has been found in the present work that under 20,000 atmos. paraffin wax may become more rigid than Bessemer steel.

The first criterion is usually modified, therefore, so as to predict rupture when the tension alone, instead of either tension or compression, exceeds anywhere a critical value.

The first type of test has its most direct bearing on the maximum tensile stress criterion of rupture. In these tests cylinders were exposed to pressure over the curved surface

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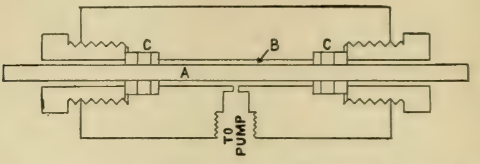
* Kahlbaum, Roth, und Seidler, *Z.S. Anorg. Chem.* pp. 29–30, 254–294 (1902).

only, the ends being left unsupported. Fig. 1 illustrates the manner of applying pressure. The rod A, the subject of the test, passes completely through the cylinder B, projecting at either end through the packing rings C. The cylinder is connected to the pressure-pump through the indicated connexions and stress applied to the test specimen by the pressure of the fluid in the annular space between the specimen A and the interior wall of the cylinder. The specimen fails by separation of the particles across some plane perpendicular to the axis, the two disconnected ends of the specimen being expelled with violence through the packing rings. The fracture does not take place at the packing rings as might be expected, but, whether for brittle or ductile materials, takes place at some point well between the rings. The nature of the process of rupture is evidently merely that of squeezing the rod out sidewise. This type of rupture may therefore be referred to as the "pinching-off-effect." There is no longitudinal stress except that due to the friction of the packing, and this a stress of compression rather than one of tension, so that here we actually have the fibres separating against the direction of stress.

Fig. 1.



Apparatus for producing the "pinching-off" effect, that is, separation of the longitudinal fibres by the application of pressure to the curved surface of a cylinder. The specimen is shown at A, the fluid exerting the pressure by which rupture is produced is contained in the annular space at B.

The nature of the fracture varies with the material. In the case of a rod of mild steel, the rupture looks very much like that of an ordinary tensile break, except that the necking down is likely to be a little more abrupt. Pl. II. fig. 2 shows a photograph of one such specimen. Other soft materials such as copper or brass show the same manner of rupture. Harder materials, such as hardened chrome-nickel steel or vanadium steel, show irregular fracture, a combination of necking down and of slip on shear planes at approximately 45° to the axis. Glass-hard tool-steel, on the other hand, shows a clean break at right angles to the axis without necking down. In the same way it is possible to break glass rod or heavy glass tubing. The fracture is beautifully clean, exactly at right angles to the axis.

In the cases of the ductile materials, the test is complicated somewhat by the fact that after the necking down has once begun there is a tensile stress tending to pull the bar apart. But this tensile stress cannot account for the beginning of the necking down, so that the tensile stress present during the actual rupture is only an incident due to the particular form of experiment, and is not at all the true cause of the rupture. Evidently there is no such complication in the case of the brittle materials which break with no necking down.

This first type of test disposes of the maximum stress criterion, therefore, as applied to either ductile or brittle materials. It shows *a fortiori*, therefore, that this criterion cannot be applied to brittle materials in contradistinction to ductile materials, as proposed by Scoble *.

Furthermore, the yield or set point and the rupture point practically coincide. No cases have ever been observed of a bar receiving set under this type of stress without rupture. The maximum stress criterion is applicable, then, neither to rupture nor to set.

Incidentally this test disposes also of the maximum stress difference hypothesis, although more direct evidence is afforded by another type of test. The principal stresses for this first type of test consist of a compression equal to the hydrostatic pressure on all planes including the axis, and a small compressive stress due to the friction on the plane normal to the axis. The maximum stress difference is equal to the hydrostatic pressure decreased slightly by the amount of the friction. In the similar case of a bar ruptured by tension, the maximum stress difference is equal to the tension. If the maximum stress difference theory holds, therefore, the "pinching-off-effect" should be produced by a hydrostatic pressure equal to the tensile strength in pounds per square inch. As a matter of fact, the stress to produce rupture always exceeded this by 25 or 50 per cent., except for the glass, when the condition was more nearly fulfilled.

Rupture of the first type has been encountered repeatedly in all this high-pressure work. It is the greatest hindrance to making connexions of any sort from the outside with the interior of a high-pressure cylinder, particularly when connecting one cylinder to another by tubing, or leading electrically insulated electrodes into the interior of the cylinder. Possible rupture of this sort has been the greatest element of danger in this work. On one occasion a specimen 5/16 in. diameter and 3 in. long penetrated 5 inches of wood driven by a pressure of only 6000 atmos. This effect might very probably produce serious consequences for one designing apparatus for the highest pressures without previous experience at lower pressures. The effect is insidious because of the unexpected ways in which it may appear.

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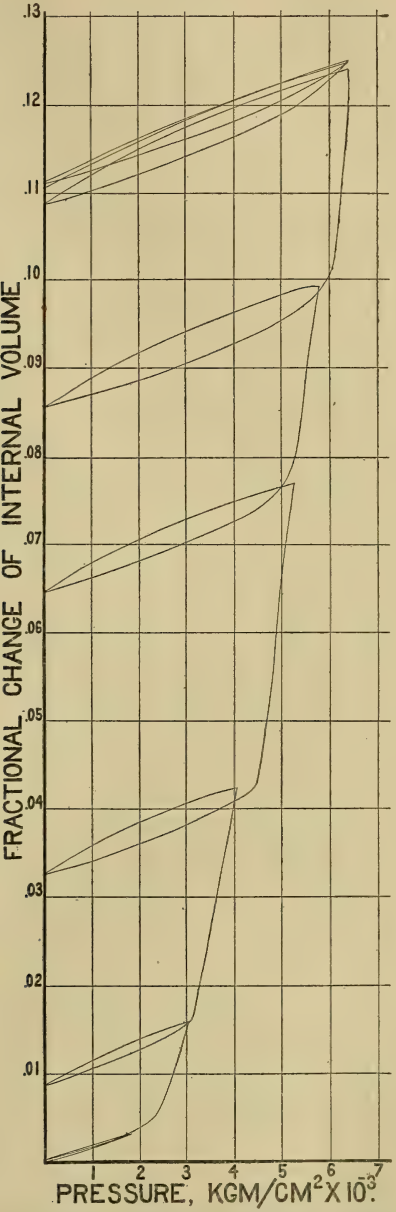
* Scoble, Phil. Mag. xix. pp. 908–916 (1910).

The second type of test is very similar to the first in the manner in which stress is applied, but diametrically opposite in its effects. The material for these tests is in the shape of a hollow cylinder, closed at the ends, and subjected to hydrostatic pressure over the entire external surface, on the ends as well as on the curved part of the surface. The tendency of the stress, as is well known, is to collapse the cylinder if the walls are comparatively thin. Such tests are familiar to engineers; the tube folds in on itself in two, three, four, or more creases, depending on the dimensions of the tube originally and on the very slight departure from perfect geometrical symmetry. That there is collapse at all must evidently be due to some slight geometric imperfection. If the tube is made heavier, however, so that geometric irregularities have less effect, the tube does not show collapse by folding under pressure, but shows behaviour of a different sort, depending on the material. Tests of this sort do not seem to have been made hitherto, or at least are not well known, probably because the pressure required to produce the effect is fairly high.

If the material of the cylinder is a ductile metal like mild steel or copper, the effect of the pressure is to close up the hole uniformly, the cylinder retaining its geometric figure. Rupture is never produced in a test of this kind, the hole eventually closing up perfectly tight if the pressure is pushed far enough. This is perhaps as one would expect; the interesting feature of this method of testing is the enormous raising of the elastic limit that it is possible to produce, and the unusual stress-strain relation below the yield point. At one time tests were made simultaneously on seven such hollow steel cylinders. The upper ends of these cylinders were led out of the pressure chamber and connected to graduated glass capillaries. The interior of the cylinders was filled with mercury, so that by observing the rise of mercury in the capillary it was possible to follow the change of internal volume with pressure. No change of length accompanies the closing of the hole, so that the rise of mercury in the capillary gives directly the change of internal volume with pressure. Fig. 3 shows a typical diagram of

Fig. 3.



Shows the relation between internal volume and pressure of a cylinder strained beyond the elastic limit by the application of pressure over the entire external surface.

the test for one cylinder. Pressure was successively applied and removed, each maximum being greater than the preceding maximum. The diagram shows distinctly the location of the yield-point, and shows also that with every application of pressure the new yield-point is not reached until the previous maximum has been passed. This of course is only a verification of common experience as to the possibility of hardening by overstrain. But former experiments on hardening by overstrain have usually been with tensile or compressive or torsion tests, where the possible raising of the yield-point is restricted in amount, a rise of 50 per cent. being large. Here, in these collapsing tests, the possible raising of the yield-point seems to have no limit except that set by the complete closing up of the hole. In the diagram shown above the yield-point has been raised about six-fold ; in similar tests with copper, where the complete process has been followed to complete closing of the hole, the yield-point has been raised ten-fold, from 1000 to 10,000 atmos. This was unexpected ; one might naturally expect a raising of the yield-point to two or three times the original value, but after this the metal might be expected to flow uniformly towards the centre like any viscous fluid.

The experiments with copper also showed the manner in which the yield-point is connected with flow. The maximum pressure reached in any cycle, plotted against the internal diameter, gave a nearly straight line extending from the original diameter at zero pressure to zero diameter at 10,000 atmos. That is, for equal increments of the yield-point, the diameter decreases by equal amounts. One might expect perhaps that the diameter would tend to decrease more rapidly at the higher pressures. The material of the cylinders after these tests remained perfectly homogeneous, without fault of any kind. Microscopic analysis has failed to reveal anything of interest except a slight elongation of the grains in the direction of flow.

The diagram shows interestingly one other variation in the normal behaviour of metal under high pressure, which is mentioned because of its intrinsic interest, although the bearing on theories of rupture is not so immediate. This is the unusually large hysteresis which goes with the raising of the yield-point. The mere existence of hysteresis as an effect apart from "Elastische Nachwirkung" has even been questioned by some. A diagram like the present shows unmistakably the possibility of this effect entirely apart from any elastic-after-effects. It also suggests that the hysteresis may in some way be connected with an unstable configuration of the molecules set up in the metal by the overstrain. In the case of ordinary metals, where hysteresis appears before the yield-point of the metal as a whole has been reached, hysteresis is probably connected with local yield in the neighbourhood of the larger or more unstable crystalline complexes of the metal.

The application of all this to theories of rupture is immediate. It suggests, in the first place, that there is no necessary connexion between the yield-point and the rupture-point. Engineers, after some discussion, seem to have accepted the yield-point as the best criterion of rupture. The reason seems to be that the yield-point and the rupture-point are fairly close together, the yield-point is pretty definitely located, and it is possible to calculate the relation between stress and strain up to the yield-point and so to find a criterion at least for yield, if any exists; whereas it is well known that the usual relations between stress and strain break down in the region of viscous flow between the yield- and the rupture-points. Here, in these tests, there is a yield-point but no rupture-point at all, so that certainly, even if a criterion were found for yield, it could not be extended to rupture.

These tests further show that the maximum stress difference criterion of yield is no more valid than the maximum stress difference criterion of rupture. For if the distribution of stress in the cylinder be calculated on the maximum stress difference hypothesis, it will be found that the hole in the cylinder will never close up under any pressure, no matter how large. The mathematical solution of this problem is given in another paper in which this whole question of the collapsing of cylinders is taken up much more in detail*. The solution assumes that the maximum stress difference condition holds throughout the entire extended process of yield. To account for the observed complete closing of the hole it is necessary that the greatest stress difference which the metal can support become less in the last stages of yield. To inquire whether the initial yield always occurs at a definite stress difference would be of little avail, for it is well known, that even for the ordinary tests of engineering the material must first be put into a state of ease by subjecting it to considerable stress. If it is not so subjected to preliminary stress, it may show yield or departure from Hooke's law at values of the stress very much lower than normal. But in tests of this type there is no natural limit to the stress which shall be used to put the cylinder in a state of ease, and since the diagram shows plainly that the beginning of yield is not sharply defined, there is here no possibility of a natural initial yield-point to which a criterion might be applied.

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* Phys. Review, xxxiv. pp. 1–24 (1912).

So far this collapsing test has been discussed only in its application to ductile materials like copper or steel. The behaviour of a brittle material like glass under the same conditions is strikingly different. Cylinders of glass made of heavy capillary tubing sealed at both ends, and hollow spheres with thick walls, have been subjected to hydrostatic pressure up to 24,000 atmos. No permanent measurable change is produced, there being neither crushing nor alteration in the dimensions of measurable amount. It should be said, however, that there must be some slight amount of flow and of interior adjustment to the pressure, although too small to measure, because several of the glass cylinders have broken spontaneously several weeks or even months after the release of pressure. Others have been kept without fracture for a couple of years. One would expect that under the conditions of this test the glass would be crushed. This is the case if the cylinder has not been carefully annealed or if it is geometrically imperfect; the material may then be reduced to an almost impalpable powder. This complete destruction of the minutest fragments of the glass apparently is because the wave of expansion, travelling through the mass after the break has started, at any point is of such intensity that every minute portion is reduced to powder by its own inertia.

For a brittle substance like glass which shows no flow we may calculate the distribution of stress by the ordinary theory of elasticity. It is thus found that the maximum stress difference will occur at the inner surface of the cylinder, and for a thick cylinder will be equal in amount to the external hydrostatic pressure. We have already seen that if the maximum stress difference criterion were valid, the greatest stress difference that the material could support would be equal to its tensile strength. Therefore since the tensile strength of glass is seldom as high as 7000 lbs/in^2, we should have had crushing under the conditions of the test at a hydrostatic pressure no higher than 7000 lbs/in^2, if the maximum stress difference theory were valid for brittle substances. But fifty times this value has been reached without rupture.

The result of this experiment with the glass seems even more unexpected than that with the ductile materials. With the metals we have at least the rearrangement of the grains produced by the flow as a basis for the raising of the elastic limit, but in a perfectly amorphous substance like glass, which shows no alteration of shape, we have evidence of no such internal change to account for the increase in strength. The experiment suggests a difference between the mechanism of yield and the mechanism of rupture. One can perhaps see why rupture should not occur in the case of the glass cylinders, since there is no place for the fragments to go to in the case of rupture, no way for the rupture to get started. But the same considerations would seem to show also no possibility of yield towards the centre. Yet yield toward the centre does get started and rupture toward the centre does not get started ; there must be some essential difference between the two.

These collapsing experiments also dispose of one other criterion of yield or rupture, better treated by the third type of test. This is the third criterion mentioned above, namely that rupture or yield will occur when the extension in any direction exceeds a critical value. If the strain is calculated in a cylinder exposed to hydrostatic pressure over the outside, the radial strain is found to be an extension at the inner surface. In the case of the ductile materials which flow toward the centre, this radial extension increases enormously with increasing flow, always without rupture or separation of the fibres in the direction of elongation. And in the case of glass under 24,000 atmos, where there is neither rupture nor flow, the elongation at the centre is greatly in excess of the elongation at rupture in an ordinary tensile test, and therefore in excess of the supposed critical elongation.

The third type of test is concerned with the rupture of heavy cylinders by internal pressure. The ordinary theory of the bursting or yield of cylinders under internal pressure is well known. At the inner surface the stress is a pressure on planes at right angles to the radius, and a tension on planes including the axis and radius ; the corresponding strain is a circumferential elongation and a radial compression. At the inner surface the stress difference, the principal stress, the principal strain, and the strain difference all have their maximum values. On any theory of rupture, then, rupture would be expected to start at the inner surface. The precise value of the theoretical bursting pressure depends on the criterion accepted for rupture. If the principal stress criterion is accepted, rupture will occur when the hydrostatic pressure is equal to the tensile strength ; if the maximum elongation is accepted, rupture will occur for a material like Bessemer steel at an internal pressure about 4/5 of the tensile strength.

The fact is, however, that for the ordinary materials of engineering practice rupture begins at the outside and runs in towards the centre. This rupture may take place either by tearing apart of the metal in an axial plane, or else by slip on a shear plane, the fracture in this latter event running in toward the centre approximately as an equiangular spiral.

Most of these bursting tests were made on drawn bars, which were pierced with the hole first and then turned off slightly on the outside so as to be concentric with the hole. Of course the most obvious suggestion with regard to this rupture from the outside is that there were flaws in the outer skin of the drawn bar penetrating more or less deeply into the interior, and that the rupture started from one of these flaws. In order to prove definitely that this is not the case, the following test was made. A bar of Bessemer steel, $4\frac{1}{2}$ in. diameter, was turned down to 4 in. so as to remove the outer layer. From this 4 in. bar a number of rings, 4 in. in diameter and 1/8 in. square in section, were turned at regular axial intervals of about 1 in. From the bar left after cutting off the rings, a cylinder for testing was made in the usual manner about $3\frac{1}{2}$ in. o. d. and $\frac{1}{2}$ in. i. d. and 8 in. long. From the other end of the same bar a similar set of rings and a similar cylinder were turned, only smaller, the cylinder being 2 in. o. d. and $\frac{1}{2}$ in. i. d. The rings were then tested to rupture on an expanding mandrel. No trace of flaw in the steel was found; the rings expanded between 10 and 15 per cent. before rupture, and the location of the fracture was haphazard, showing no longitudinal vein of special weakness in the steel. The cylinders were then tested to rupture in the usual manner. For this purpose, where the cylinders are made of very ductile material, it was found convenient to fill the cylinders with lead instead of with a true liquid, since it is easier to keep the lead from leaking after the cylinder has begun to stretch. The lead transmits these high pressures nearly hydrostatically. Pressure was produced by a hardened steel piston forced against the lead by the ram of an hydraulic press. A cup-shaped washer of Bessemer steel prevented the lead from leaking past the piston. Because of the very great stretching it was necessary to make several strokes of the piston before rupture was produced.

The results of these two tests with the two cylinders mentioned above are shown in the photographs. The larger cylinder, Pl. II. fig. 4, broke by separation of the fibres along an axial plane. Break occurred suddenly with explosive report, so that it was not possible to ascertain whether rupture really started from the outside or not. But with the smaller cylinder, figs. 5 and 6, break started more gradually, and it was possible to watch the whole proceeding. In fact, two strokes of the piston were necessary to enlarge the crack to the condition shown in the figure after the first beginnings of the fissure appeared at the outer surface. The fissure appeared first as a small longitudinal crack, which extended itself axially, the central portion gaping wider and wider as the metal on one side protruded by slipping out along a shear plane.

These two experiments showed that the rupture, which apparently begins at the outside, is not produced there by flaws in the steel. There might still be some question as to whether the rupture really did begin at the outside, since of course it is conceivable that the slip had begun at the inside and travelled to the outside, there first becoming noticeable. That the rupture actually does begin at the outside was shown by other experiments on nickel-steel and on copper cylinders. The nickel-steel cylinders do not stretch so much before rupture as the Bessemer cylinders, so that it was possible to produce rupture of these cylinders with a true liquid transmitting pressure. That the rupture really begins at the outside was shown by the appearance of the crack on the outside and its gradual growth, just as above, without any liquid leaking through from the inside, as of course it would have done under the high pressure, 30,000 atmos, if there had been the slightest crack reaching from the centre out. The copper cylinder showed the same thing. Here it was possible by a special arrangement of shrunk-on steel rings to make the necessary connexions and produce rupture with a fluid. Rupture again appeared at the outside first, and spread toward the centre along a shear plane, leak not finally occurring until the crack had opened to the dimensions shown in the photograph, fig. 7 (Pl. II.).

One feature common to all these tests, whether the rupture through the mass of the metal takes the form of a tearing of the fibres or a shear, is that at the inner surface the break is always along a shear plane for a short distance. If the rupture from the outside is by tear, at the inside there are almost invariably two shear planes, running down into the tear. The result is that a sliver of metal in the form of a triangular prism is expelled through the crack. This sliver has been caught on several occasions in a block of lead. It is difficult to see how this shear along two planes could get started if the crack originally started from the inside. Evidently the crack runs in from the outside until so close to the centre that the prism slips into the crack, driven by the high internal pressure. This universal manner of rupture affords additional evidence, in those cases where the rupture occurs so suddenly that it cannot be observed, that the crack starts from the outside.

The particular bearing of this third type of test on the theories of the conditions of rupture is in showing that the maximum extension criterion does not hold, although of course all the other criteria are also ruled out, if the stress-strain relation is calculated up to the rupture-point by the ordinary theory, because every one of the supposed critical quantities has its maximum value at the inner surface. But the striking feature of all the tests is the enormous stretching of the inner surface without rupture. The Bessemer-steel cylinders of Pl. II. figs. 4 and 5 show a circumferential elongation at the inner surface of 175 and 125 per cent. respectively. The tool steel cylinder of fig. 8 has an interior elongation of 120 per cent. The copper cylinder of fig. 7 shows an interior elongation of 300 per cent. and the lead cylinder of fig. 9 several thousand per cent. There does not seem to be any connexion between the value of the elongation at the exterior surface, where rupture actually does occur, and the elongation under pure tensile tests at rupture. We may have values either greater or less than the tensile elongation. The nickel steel cylinders, those of specially toughened steels, the copper cylinders, and the 3 in. Bessemer cylinder all showed a circumferential elongation at rupture very much less than the elongation at rupture under pure tension. The 2 in. Bessemer cylinder showed an elongation almost exactly equal to that showed by the rings cut from the same piece, while a drawn tube of annealed steel has shown an elongation of 100 per cent. at the outside, and the lead cylinder shows 300 per cent. The tensile value for the steel is about 20 per cent., and for the lead 25 per cent.

Tests on brittle materials like glass also show that the maximum elongation criterion is not fulfilled. Of course, in the case of a brittle material like glass, rupture comes so suddenly and is so complete when it does come that it is impossible to tell by any examination of the fragments whether rupture began at the inside or the outside. But the maximum value of the stress which the glass is capable of standing before rupture is considerably in excess of the theoretical limit. On no theory ought the glass to be able to stand more pressure on the inside than the tensile test limit, even if the walls of the cylinder are of infinite thickness compared with the bore. One can in cases like this, where there is no yield up to the rupture-point, safely apply the theory of elasticity in calculating the strain up to the rupture-point. This means that no glass capillary ought to be able to stand more than 500 atmos. Capillaries have been found, however, which have successfully withstood 1000 atmos. The question of annealing is of great importance here. Probably with more careful annealing it would be possible to exceed this limit. In any event, the circumferential extension, even when the pressure is only 1000 atmos., must be nearly twice the critical value under rupture in tension.

The manner of rupture described here, beginning at the outside first, is not universal for all materials, but probably holds only for those materials showing considerable plasticity, There can be little doubt but that the rupture of glass cylinders does begin at the inside, and one case in another substance has been actually observed in which the rupture did travel from the centre to the outside. A cylinder of transparent gelatine, about 1 in. o. d. and cast with a concentric hole $\frac{1}{16}$ in. diameter, was ruptured by blowing into it. The rupture took place exactly as the theory predicts ; it started at the inner surface as a tear across an axial plane, and travelled out slowly toward the outside as the interior was more and more distended by blowing.

It is worth while examining these bursting tests a little further, for in this case we can make plausible to ourselves why rupture does not occur at the inside, and so gain an inkling of a much more general criterion than any of those hitherto proposed which must always be satisfied when rupture occurs. If we consider the state of stress at the inside surface we shall find that initially as long as the equations of elasticity hold, the stress consists of a pressure across planes perpendicular to the radius, and a circumferential tension which is greater than the pressure. When the internal pressure becomes too great, however, the inner layers yield plastically, the hole taking a set. During this plastic yield the metal must be thought of as behaving like an imperfect viscous liquid, tending to transmit pressure hydrostatically in every direction. In consequence of the tendency to equality of stress in every direction, the initial circumferential tension becomes a circumferential compression. The mean stress, therefore, at any point of the interior surface becomes a compression after the plastic yield begins, whereas before yield the mean stress was a tension, because the circumferential tension was greater than the radial compression. The strain, then, after yield, consists of a volume compression at the inner surface, whereas before yield there was a volume extension. Consider now what would happen at the inner surface if rupture were to get started there. We are to think of the general action of rupture as one relieving the stresses at any point, for otherwise the rupture would have no excuse for existence. Before plastic yield, then, rupture at the inner surface would result in release of the volume distension, that is, the volume of the steel would become less. As a result, the compressing liquid would have room to become greater in volume, and the pressure would automatically fall. But if the rupture were to start after the plastic yield, that is after volume compression had taken place at the interior surface, release of the pressure would result only in increase of volume of the steel, the compressing liquid would lose volume, and the pressure would as a result be increased instead of decreased. In this case, rupture, instead of affording relief from the existing state of affairs, would only intensify them. That is, rupture would be an explosive affair, during which work was done against the applied forces instead of by them. This is opposed to all experience. This simply means, then, that even if rupture on a small scale should start at the interior surface during the state of plastic yield, it would be unable to spread. If rupture is to start at the centre and travel out it must start before the stage of plastic yield is reached.

The photograph of the 4 in. Bessemer-steel cylinder, fig. 4, shows this most strikingly. The interior surface is covered with numerous slip bands, some of them very prominent. where the rupture had started but was unable to spread, The pressure on the plastic metal at the inner surface has been so high that a process similar to cold-welding has gone on. The crystalline grains were probably torn apart so as to slip past each other, but the pressure was great enough so that the separation was never beyond the range of molecular attraction, and true rupture did not occur. The copper cylinder also shows the same slip bands at the interior surface.

Another interesting question in this connexion is that of the greatest possible raising of the elastic limit by permanent stretching. It is easy to see that the stress distribution in such a cylinder after the yield-point has been passed and the pressure released is exactly like that in a gun with shrunk-on hoops. One might expect, then, to be able to reach a pressure about twice that of the yield-point under pure tension, but as a matter of fact it is possible to exceed this, because of the hardening of the metal by over strain. Thus a copper cylinder, originally $\frac{1}{8}$ in. i. d. and 3 in. o. d. has been subjected to 10,000 atmos. without the yield extending throughout the entire mass. The inner hole has been stretched about 50 per cent. by this pressure. Pressures of 30,000 atmos. have been reached in cylinders of soft nickel steel or of tool steel, and of 40,000 in a cylinder of hardened nickel-steel. But the hardening process by over load is not nearly so complete or thorough as it is for cylinders collapsed by external pressure. The yield under high pressures continues for a very much longer period of time, and the raising of the elastic limit after complete disappearance of set is not permanent. After a period of rest, yield is likely to begin again at a pressure lower than the former maximum. Thus a cylinder of soft nickel-steel, originally 8 in. o. d. and $\frac{5}{8}$ in. i. d., had had the elastic limit apparently raised to 28,000 atmos. by repeated applications of pressure which stretched the inner hole from $\frac{5}{8}$ in. to $1\frac{1}{8}$ in. But now, after several years of use, it is unsafe to subject this same cylinder to more than 15,000 atmos. The initial yield-point of the cylinder was about 8000 atmos.

Summary.

In this paper the results of three types of tests with high hydrostatic pressures have been described in their bearing on theories of rupture. The tests of cylinders under pressure on the curved surface only ("the pinching-off-effect") show that the maximum principal stress criterion is not valid. The tests of hollow cylinders under external pressure show that neither the maximum shear stress nor the maximum shear strain criterion is valid, while the tests on the bursting of heavy cylinders under internal pressure show that the maximum elongation criterion is not valid. These conclusions apply to both brittle and to ductile materials. The tests do suggest that there may be some essential difference between a ductile and a brittle material (more generally between a crystalline and an amorphous one), but show that the distinctions proposed hitherto cannot hold. It is suggested that in every case there must be some more general condition satisfied than those usually considered. There is not enough material at hand to enable a formulation of the condition to be made, but the considerations with regard to the bursting of cylinders under internal pressure point out what the general nature of the conditions must be. Any entirely general criterion of rupture must demand, among other things, that there be a free space to contain the fragments when rupture occurs, and must also demand that the nature of the rupture be such as to relieve the applied stresses.

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VI. *The Earth's Magnetic Field*[*]. *By* W. F. G. SWANN, *D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield*[†].

A LARGE amount of work relating to the earth's magnetic field has been done by Prof. Schuster, who by a critical analysis of its form has deduced several important facts with regard to its cause and variations. The present paper, while not definitely formulating a theory to account for the field, comprises a discussion as to the possibility of its explanation, as a phenomenon arising out of the rotation of the earth. In order not to encumber the paper with mathematical analysis, such work whenever possible has been relegated to an appendix, the results of the analysis only being quoted in the paper.

The first idea that suggests itself is that of the rotation of a surface charge, but the horizontal magnetic field at the equator of a sphere of radius a, rotating with angular velocity ω, and charged to a potential V is (see appendix, Problem 1) $\frac{V\omega}{3}$, a result depending only on the angular velocity, and independent of the size of the sphere, for a given potential.

A more hopeful basis is to be found in the view, that each volume element of the earth contributes a portion to the field, as a result of its rotation. In this case, the fact that the volume of the earth depends on the cube of its linear dimensions insures that a very small contribution by each cubic centimetre of matter shall give rise to an appreciable effect on the earth's surface, in spite of a possible variation of the effect according to the inverse square law of the distance.

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[*] While the present paper was being written a note came into my hands of a presidential address recently given by Professor Schuster before the Physical Society of London, and judging from that note, it is possible that the grounds covered in the address and in the present paper may to some extent overlap.

[†] Communicated by the Author.

The manners in which the volume elements of the earth may give rise to a magnetic effect may be classed under three heads.

(1) The rotation of the earth may give rise to an ordinary current, involving motion of electricity relative to the volume elements themselves.

(2) Each volume element may act as though it were charged, or the rotation may result in some kind of radial distribution of the charge.

(3) Each molecule of the earth may be looked upon as equivalent to a very feeble magnet, owing to want of complete compensation of the magnetic fields due to its orbital electronic motions, and the rotation of the earth may bring about an orientation of these molecular magnets in favour of one direction. The only advance of such a theory over an assumption of permanent magnetization would be in its attempt to seek in the rotation itself a reason for the orientation required.

Any theory which is to explain the earth's magnetism as arising from its rotation must be restricted to some extent by the following conditions:—

(1) It must provide for the absence of any large effect due to the earth's translatory motion in its orbit, since such an effect would be different along the line of the earth's motion to what it is in a direction perpendicular thereto, so that a large diurnal variation in the magnetic elements would result.

(2) It must be of such a nature as to predict no appreciable magnetic field in any laboratory experiment in which a sphere of moderate size rotates with a reasonable angular velocity, as such fields would not escape detection.

(3) It must account for the fact that the sun, rotating with its known angular velocity, produces no appreciable field at the earth. Such a field would, owing to obliquity of the ecliptic, give rise to a large diurnal variation in the magnetic elements.

(4) It must not be of such a type as to lead to an enormous field at the sun's surface, due to the rotation of that body, since it may be certain that a field for example of the order of 2000 C.G.S. units would have been detected by the Zeeman effect in the sun. Such an effect would be distinguishable from the effect observed in the sun spots in that it would show a regular variation over the sun's disk.

There is a certain amount of elasticity in the conditions which these restrictions impose, in view of the great differences in the temperature of the bodies dealt with, but they nevertheless serve as a useful guide in the formation of a theory. It may here be mentioned, that if the sun has a magnetic field, a knowledge of the magnitude of that field at its surface would be most helpful in the formation of a theory, as it would, when considered in conjunction with the earth's field, to a large extent decide how the field due to a rotating sphere varies with its dimensions and its angular velocity.

Considering the first theory, which attempts to account for the magnetic field as due to the existence of an ordinary current brought about by the rotation, we have to realize that the motion of any particle of the earth may be looked upon as consisting of a linear velocity, compounded with an acceleration directed towards the earth's centre, and it is in terms of these quantities that the current density must be expressed. The spacial derivatives of these vectors may also be involved, if the current is to be looked upon as in any way dependent on the relative velocities of the different parts. The current density may be written in the form

$$\sigma=\sigma_1+\sigma_2+\sigma_3+\sigma_4,$$

where σ_1 represents all terms involving the acceleration only, σ_2 represents all terms involving the velocity only, σ_3 represents terms involving products of powers of the acceleration and of the velocity, and σ_4 represents terms involving only the single spacial derivative ω, *i. e.* the angular velocity.

It is interesting to consider the currents represented by each of these terms, and to see how far we can, from general principles, restrict them.

Consider the contribution of the first term, and to fix our ideas, let us take the case where σ_1 is proportional to the centripetal acceleration f. This case is worked out in the appendix (Problem 2), and gives $\frac{4}{15}\pi\sigma_0 a^2\omega^2$ for the horizontal magnetic field H at the equator of a sphere of radius a, σ_0 being the current density one centimetre from the axis of rotation, for unit angular velocity.

Let suffix m refer to a sphere of 10 cm. radius, rotating 10 times per second, suffix e to the earth, and s to the sun. Then taking $a_e=6\times10^8$ cm., $\mathrm{H}_e=0{\cdot}3$ C.G.S. unit, we have

$$\mathrm{H}_m=\frac{a_m^2\omega_m^2}{a_e^2\omega_e^2}\mathrm{H}_e=0{\cdot}6\times10^{-4}\text{ C.G.S. unit},$$

a value too small to be readily detected in a laboratory experiment.

The value of $\omega_s a_s$ is about four times the corresponding value for the earth's surface, so that H_s would be about 5 electromagnetic units, an amount far too small to detect by the Zeeman effect. The field produced by the sun at the earth would be negligibly small.

The term σ_1 cannot contain a part of appreciable importance, involving a higher power of f than the first, for if it involved the second power for instance, it is easy to see that H would be proportional to $\omega^4 a^3$, in which case H_m would amount to 2·4 electromagnetic units, a quantity far too large to have escaped detection.

Considering the term σ_2, we cannot at once predict its absence from the fact that the earth's translatory motion must give rise to no appreciable field; for even if terms of this type did exist, the earth's translatory motion would presumably not result in a magnetic field, since any tendency to produce a current along the line of motion of the earth would simply result in an electrostatic displacement parallel thereto, such as to balance that tendency. A similar remark applies to any terms involving the radial acceleration of the earth towards the sun, which terms but for this cause would be of considerable importance, since the radial acceleration in question amounts to about 0·2 of the acceleration of a point on the earth's surface towards its centre.

If we accept the principle of relativity, we must conclude that in uniform translatory motion there is no electrostatic distribution of the kind above mentioned, and consequently no tendency to produce a current along the line of motion. On this basis the term σ_2 must be discarded.

With regard to the terms of the type σ_3, it is easy to see that the expressions to which such terms lead, as far as their dependence on ω and a are concerned, only differ, in general form, from those resulting from terms of the type σ_1 in that they contain additional powers of ωa. The value of ωa for the sun is not sufficiently different from the corresponding quantity for the earth to provide us with any information further than that provided in the case of terms of the type σ_1. Again, the presence of additional positive powers of ωa only reduces the magnitude of the field which we might expect to obtain in a laboratory experiment on the rotation of a small sphere, so that we must be prepared to admit the presence of terms of the type σ_3.

Considering terms of the type σ_4, which correspond to a constant current density of the form $\sigma = F(\omega)$ where $F(\omega)$ is some function of ω, we find, on working out the field at the equator of a rotating sphere (see appendix, Problem 3) that H is proportional to $aF(\omega)$. Thus, even considering a case where only the first power of ω is involved, the field is proportional to ωa, and according to this a sphere of 10 cm. radius rotating 10 times per second should give rise to a field at its surface amounting to one-seventieth of the earth's field, a quantity far too large to have escaped detection. We are thus restricted to terms of the forms σ_1 and σ_3 in the expression for σ. A term of the type σ_1, proportional to the radial acceleration *f*, gives rise, as we have seen, to a field at the equator given by $H=\frac{4}{15}\pi\sigma_0 a^2\omega^2$. The current density $\sigma_0 a\omega^2$, which must exist on the equator at the surface, in order to account for the earth's field, thus amounts to 7×10^{-10} electromagnetic unit.

It is easy to see that a term of the type σ_3, proportional to the product of the velocity and of the radial acceleration, would require a current density on the equator of the same order of magnitude.

Although 7×10^{-10} C.G.S. unit is a current of an order readily detectable by a galvanometer, we could not of course detect the earth current in question in this way, for a very little consideration will show that, even if the current existed in the earth's crust, we could not control the direction of its flow so as to make it curl round the coils of a galvanometer.

At first sight the permanent existence of such currents would seem at variance with reason, in view of the apparent necessity for the rapid conversion of their energy into heat owing to friction; but in examining the question it is necessary to take a closer view of the matter than one involving considerations of resistance, viscosity, &c., and to look upon the permanent existence of these currents, if they do exist, as one of the necessary conditions for that fine-grained dynamical equilibrium of matter, the elucidation of which must necessarily involve the explanation of viscosity and resistance themselves in its scope. When this attitude is adopted, the hypothesis for the existence of such currents falls well within the range of possibility.

There are two obvious ways in which we may imagine such a current to come about. Suppose that we admit that, in ordinary matter, corpuscles do occasionally leave the atoms and join those corpuscles which exist between them, the balance being kept up by a re-absorption into the atoms of similar corpuscles; then, if the rotation results in a very slight want of symmetry, fore and aft, in the rate of expulsion of these electrons, if we have, for example, an increase in the rate of expulsion to the fore, and a corresponding increase in the rate of absorption to the rear, we have an explanation of the current, and the extremely small order of the effect necessary may be gathered from the following consideration.

To fix our ideas, suppose an atom emits a corpuscle $2p$ times per second, with a velocity of 10^7 cm./sec. For a resting molecule there is no resulting current, because the emission is perfectly symmetrical. Suppose, however, that owing to the motion of the matter, the emission p in the direction of motion is altered in favour of that direction by a fraction k of its value. The effect will be equivalent to a current density of the order of magnitude $\sigma = kpNe\lambda \times 10^7$, where e is the electronic charge, and is equal to 10^{-20} E.M.U., λ the mean free path of a corpuscle, and N the number of atoms per c.c. Taking $N = 10^{23}$, and $\lambda = 10^{-7}$ cm., we see that in order to obtain a current density of 10^{-9} E.M.U. it is necessary to have $kp = 10^{-12}$. Now k must be a function of the centripetal acceleration, and of the velocity v of the element of matter, and even though, to satisfy the conditions of uniform translatory motion, we imagine it to be of such a form as to contain no terms of the type v/C or v^2/C^2 (C being the velocity of light), or at any rate of such a form that the other alterations in the matter brought about by the motion prevent any such terms appearing in the final expression for the magnetic field, we may nevertheless expect terms of the order f/C, fv/C^2, &c. to occur.

Considering a case where k is of the order f/C, *i. e.* 10^{-10}, we see that it is not necessary that p should be greater than 10^{-2}, so that the expulsion of one electron from an atom in 100 seconds would be sufficient to ensure that the *variation* in this quantity, resulting from the motion, would account for the earth's field.

In spite of the smallness of the necessary value of p, it may be argued that it would correspond to a very radioactive substance, since one gram of radium only expels 10^{10} corpuscles in one second. It must be remembered, however, that we are not here dealing with the complete expulsion of corpuscles from the matter. The chance of a corpuscle leaving an atom, due to the comparatively large pull exerted by an adjacent atom, and remaining in the vicinity of the atoms, is enormously greater than the chance that the corpuscle will get away altogether, so that the above values of p must not be looked upon as being inconsistent with radioactive phenomena. Indeed, values of p enormously greater than that which it has been necessary for us to assign are tolerated, for example, in the particular theory of metallic conduction which explains the phenomenon of conduction as due to a kind of polarization of the conductor by the electric field, resulting in the atoms pulling corpuscles out of their neighbours to a greater extent in one direction than in another (see J. J. Thomson, 'Corpuscular Theory of Matter,' p. 86). The expression for the electrical conductivity i comes out as $i=\frac{2}{9}\frac{e^2dp'nb}{\alpha\theta}$, where e is the electromic charge, d is the distance between the two charges constituting the doublet which represent the atom, n is the number of molecules per c.c., $\alpha\theta$ is the mean kinetic energy of a gas molecule at a temperature θ, b is the distance between the centres of the doublets, and p' is the number of corpuscles emitted by a doublet per second. Taking $\alpha\theta=5\times10^{-14}$, $e=10^{-20}$ E.M.U., $d=10^{-8}$, $b=10^{-8}$, $n=1{\cdot}6\times10^{23}$, $i=0{\cdot}6\times10^{-3}$ C.G.S. unit (for silver), we readily find $p'=10^{17}$, *i. e.* a quantity 10^{19} times as great as that which we have allowed ourselves in the case of the quantity p.

The current may be accounted for without bringing the question of the expulsion of electrons from the atoms into the matter. Let us confine our attention to those free electrons which exist between the atoms: in the case of a piece of matter in the resting state the average velocity, and the mean free path, are independent of the direction. If the matter be in motion, however, we may expect that these quantities will vary according as they are considered in the direction of motion of the matter, or in the opposite direction. The chances are that any dynamical scheme applicable to the electron will lead to this result. Truly, with the electrons considered as hard spheres, and with ordinary Newtonian dynamics as applied to them, there is no apparent foundation for such a belief, but the application of Newtonian dynamics in its simplest form, involving as it does forces between the electrons depending only on their relative positions, and masses independent of the motions, is only an approximation to the true state of affairs. In fact, even in the case of uniform translatory motion, the principle of relativity itself involves a want of symmetry in the velocities, for example, of the kind here suggested, as may readily be seen by considering the case of a particle which, in a resting system, oscillates backwards and forwards between two points whose x coordinates are x_1 and x_2. If the time t_1 taken by the particle in going from x_1 to x_2 is the same as the time taken in going from x_2 to x_1, and if x_1' and x_2' refer to the corresponding system moving parallel to the axis of x with velocity v, then, writing ϵ^{-1} for $1-v^2/C^2$, it can be shown that the time taken by the corresponding particle in going from x_1' to x_2' is $\epsilon^{1/2}t_1+\frac{\epsilon^{1/2}v(x_2-x_1)}{C^2}$, but the time taken in going from x_2' to x_1' is $\epsilon^{1/2}t_1-\frac{\epsilon^{1/2}v(x_2-x_1)}{C^2}$. Thus, not only is the average velocity altered, but the alteration depends on the direction. In the case of uniform translatory motion, however, the principle leads to the result that, on the whole, the various motions so adjust themselves that, if a piece of matter at rest produces no magnetic field, that piece of matter will produce no field when in uniform translatory motion. It is reasonable to suppose, however, that in cases other than those of uniform translatory motion this compensation will not necessarily be exact. If n is the number of corpuscles per c.c., V the average velocity of a corpuscle, λ the mean free path, t the time which elapses between two collisions, s the number of collisions suffered by a corpuscle per second, and if further, suffix (1) refers to the direction of motion of the element of matter, and suffix (2) to the opposite direction, the resultant current density due to the want of symmetry referred to is of the order

$$\sigma=nes(V_1t_1-V_2t_2)=nes(\lambda_1-\lambda_2)=nes\delta\lambda,$$

where $\delta\lambda=\lambda_1-\lambda_2$.

Since $s\lambda=V$ we may write $\sigma=neV\delta\lambda/\lambda$.

Taking $n=10^{24}$, $e=10^{-20}$ E.M.U., $V=10^7$ cm./sec.*,

we find that, in order to produce a current density of 10^{-9} E.M.U., we must have $\delta\lambda/\lambda=10^{-20}$. Now the first term which we might expect to be involved in the expression for $\delta\lambda/\lambda$ is a term of the order f/C, since terms independent of the acceleration, and depending only on the velocity, must not exist, owing to the fact that they would involve magnetic fields for matter moving with uniform translatory velocity. f/C is of the order 10^{-10} however, *i. e.* far greater than we require. Indeed, a term of the order $(f/C).(v^2/C^2)$, that is 10^{-18}, is amply sufficient to account for the necessary value of $\delta\lambda/\lambda$, and indeed leaves a good margin.

It may be argued that, in raising the question of the possibility of a want of symmetry in the expulsion of electrons, or in the mean free paths of the electrons, we have given no suggestion of a physical basis for the existence of such a state of affairs; and it may be asked whether the laws necessary to decide for or against the hypothesis are not already known to us, so that all that is necessary in order to settle the question is mathematical analysis. The answer to this question requires rather careful consideration. If we take the constitution of matter as entirely electrical, and following Larmor ('Æther and Matter,' chapter x.), take the electromagnetic scheme as the sole criterion for the determination of the motions of the electrons, which themselves are considered merely as singularities in the æther, there is absolutely nothing to tell us what will happen to the matter as a result of its motion, the apparent answer to the problem in the case of uniform translatory motion being, as I have pointed out in a former paper*, merely equivalent to a postulation of the effect deduced. Taking the electron merely as a singularity of the æther, the electromagnetic scheme can be satisfied by any state of electronic motions we choose to assign, so that the asymmetrical expulsion of electrons from the atom, for example, satisfies the scheme equally as well as the symmetrical one. In order to decide what happens when a piece of matter is set in motion, we must either know the motion of each electron in the molecule, at some instant, or we must devise sufficient subsidiary laws, as I have called them, to restrict the types of electronic motions which can exist, and satisfy the electromagnetic scheme, to those which it is possible for the electromagnetic scheme to evolve out of the matter as it originally existed.

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* This value of V is calculated for a temperature 0° C. by taking the mean kinetic energy of the corpuscle as equal to that of the hydrogen molecule.

The electromagnetic scheme is capable of tracing the motion of every electron in the universe for all time, provided that the complete state of motion is given at some instant; and in this sense the scheme is certainly complete if it is only true, and there is no loophole for the existence of other laws such as gravitation, as laws distinct from it. The fact that two pieces of neutral matter attract each other when they are brought into each other's vicinity is not to be looked upon as a separate law, but as a fact consistent with the scheme but not required by it. Given any initial state of electronic motions, and the electromagnetic scheme to guide them, in their future history, certain types of regularity will show themselves in the system which are not required by the scheme fundamentally, but which exist in virtue of the nature of the system originally created. Those laws, which we call the laws of nature, are the uniformities which evolve out of the system which constitutes our universe; at least this is the view which one must take of them if one starts with such a scheme as the electromagnetic scheme as a basis.

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* Phil. Mag. [6] xxiii. p. 86.

Returning to the particular problem with which we are here concerned, we must on this basis look upon the want of symmetry, if it exists, as a perfectly regular and orderly development of the electronic motions, corresponding to the rotating earth, a condition of affairs originating not as a mere chance for that particular sphere, but rather a type of regularity common to all rotating bodies. There is nothing more astonishing in the regularity of the effect, if it exists, than in the similarity of constitution of all atoms of the same element. When we start to attempt to explain the effect, we are, however, confronted with a difficulty. It is impossible for us to take cognizance of each electron in the sphere, and trace by means of the electromagnetic equations the whole of the phenomena associated with the production of motion in the sphere. We must be content with a discussion of the motions of the parts of the atom in terms of more or less approximate empirical laws, involving the conception of forces of a rather crude type between the electrons. These laws are usually formed by analogy, after the type of the laws which we find to govern the motion of matter in bulk; but in applying them to atomic dynamics we are in the rather helpless condition of being unable conscientiously to admit any such ideas as those of elasticity, viscosity, &c., as distinct from those concepts to which the dynamical laws themselves lead. We are often compelled to introduce these unexplained phenomena however, but when we do dare to admit them we usually feel that we ought, as a kind of penance, to restrict them to the same types as those which we find to hold for matter in bulk; and it is consequently not surprising to find that with such a limited means of attack, it is impossible to decide what the effect of motion on the molecules is. In fact, the whole question resolves itself into this: we have not yet sufficient experimental knowledge of the constitution of the atom to be able to devise a workable empirical dynamical scheme, applicable to the atom, and sufficiently comprehensive to predict all those atomic phenomena which might be imagined to be predicted by a being of infinite mathematical capability, who was given the complete electrical field of the universe at some instant, together with the assumption of the electromagnetic scheme (or whatever other scheme is the correct one), to trace the course of events in the universe in its future history.

In concluding the consideration of the question of the existence of the currents above referred to, it must be pointed out that it is not my intention here to either affirm, or deny, their existence, but merely to show that the chances are in favour of it, and that if they do exist, there is evidence to show that they are likely to be of an order such as to account for the earth's field, and, secondly, that there can be but little weight in an argument which denies their existence simply on the ground that the *necessity* for it is not apparently contained in any of those more or less crude forms of dynamical laws by means of which we at present attempt to correlate the electronic motions with the motions of matter in bulk.

The case of the rotation of a charged earth.

In considering the question of the rotation of a charged earth, we are at once confronted with the difficulty of explaining the absence of an enormous electrostatic field associated with it, and again, in the case of a conducting earth, we could not have the volume elements charged, the charge would come to the surface. We shall not at once discard the hypothesis for these reasons however, since, as we shall see, the difficulties are not insurmountable.

We shall consider the problem of a rotating earth, charged with a constant volume density ρ, the charge being fixed in the volume elements. The problem is one where the current density is proportional to the distance from the axis of rotation, and by a method of procedure exactly similar to that adopted for this case, we obtain $\frac{4}{15}\pi\rho\omega a^2$ for the field H on the equator. This is the field which would be observed by a stationary observer, or rather by an observer participating in the translatory motion of the earth but not in its rotation. The field which would influence a compass-needle fixed on the surface of the rotating earth may be deduced from the following considerations*.

The field inside the test magnet may be looked upon as consisting of two parts, the field H referred to above, and the field H′ due to the motion of the induced charge on the surface of the compass-needle. The electric polarization F at the earth's surface is practically uniform over the compass-needle, so that the charge on the surface of the needle would be that due to placing it in a uniform electric field with polarization F. Now imagine a large charged plate, giving a polarization perpendicular to its surface, of amount F. Imagine a compass-needle to be placed in this field, and suppose that the two are set in uniform motion, in the direction parallel to the plane of the plate with velocity equal to ωa. We know that there would be no effect on the compass-needle, so that we can conclude that the magnetic field H′, produced by the motion of the induced charge on the compass-needle, is just equal and opposite to the magnetic field $4\pi\omega a\mathrm{F}$ produced by the motion of the plate. Thus we see that the resultant field acting on a compass-needle on the earth's surface is, at the equator

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* It may be remarked that the translatory motion of the earth would give rise to a field; this part of the field, however, could not be detected by an observer on the earth, for exactly the same reason that the magnetic field due to a charged sphere for example, moving through space in company with an observer, is incapable of detection by the observer.

$$\mathrm{H}_1=\mathrm{H}-\mathrm{H}'=\frac{4}{15}\pi\rho\omega a^2-4\pi\omega a\mathrm{F}.$$

Since, neglecting a very small term of the order v^2/C^2,

$$4\pi\mathrm{F}=\frac{4}{3}\pi\frac{a^3}{a^2}\rho,$$

we have

$$\mathrm{H}_1=-\frac{16}{15}\pi\rho\omega a^2.$$

The counteracting field due to the motion of the compass-needle thus alters the sign of the charge which we should otherwise have to attribute to the volume elements of the earth in order to account for its magnetic field, the necessary charge being a positive one*. The theory makes the equatorial horizontal field at the surface proportional to ωa^2, for a given volume density, so that the field attainable by the rotation of a sphere in the laboratory would be far too small to detect. Again, the field corresponding to the rotation of the sun would amount at its equator to 200 C.G.S. units, which is too small to detect by the Zeeman effect. The order of magnitude of the volume density of electrification necessary to account for the earth's field is 10^{-14} E.M.U., which corresponds to a deficit of one electron in about 10^{18} pairs of positive and negative electrons in neutral matter.

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* [*Note added May 8th*, 1912.] While the present paper was in process of publication, Prof. Schuster's address to the Physical Society appeared in printed form. In that address, the problem here discussed is treated, and it is further pointed out, that the theory gives the wrong sign for the vertical component. This may readily be seen on the line of argument here adopted, when we realize that the motion of the magnetic needle cannot affect the observed value of the vertical component, so that the charge necessary to account for this component is a negative one. The difficulty in this respect vanishes in the modified form of the theory discussed next, in which the volume charge is balanced, as far as its electrostatic effects are concerned, by an equal surface charge. Similar remarks apply to the theory on page 93.

The electrostatic field at the surface of the sphere amounts, when expressed in electrostatic units, to 10^6. The difficulty in this respect may be overcome by imagining that, corresponding to the volume distribution ρ, there is a surface distribution of s units per sq. cm., the total amount of which is just equal to that in the volume distribution. There will then be no electrostatic field, but there will be a magnetic field, which, in virtue of the absence of the electrostatic field, will be the same for a moving as for a fixed observer*. This magnetic field will be composed of two parts, which, at the equator, comprise $\frac{4}{15}\pi\rho\omega a^2$ due to the rotation of the volume distribution and $\frac{4}{3}\pi s a\omega$ (see appendix, Problem I.) due to the rotation of the surface charge. Hence, remembering that $4\pi a^2 s = -\frac{4}{3}\pi a^3\rho$, we have $H = \frac{8}{45}\pi\rho\omega a^2$, which gives H of the same order as before.

With regard to the difficulty of explaining how the surface charge is prevented from mixing with the volume charge, it may be remarked, that the action of the centrifugal force of the earth's rotation can easily be shown to result in distribution somewhat of the kind described, and it would give the field in the right direction, but on calculating the effect, even for the most favourable case, where gravity does not pull the electrons, we find an effect of far too small an order to account for the earth's field, so that unless other phenomena, such as intense corpuscular pressure in the atoms of some part of the earth's substance, be brought to our aid, there seems little evidence in support of the distribution required.

The effect of a radial electrostatic polarization resulting from the rotation.

If we imagine that the rotation of the earth results in an electrostatic polarization in a sense perpendicular to the axis of rotation, we have a basis for the existence of a magnetic field.

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* Of course it is not necessary that the distribution shall be of the simple nature described: we might, for example, have thick concentric shells of positively electrified matter separated by thin shells of negatively electrified matter.

According to the view suggested by Sir J. J. Thomson, we may look upon the combination of the two atoms A and B as resulting from the gain by A of an electron which B has lost. Any tendency of the molecules to set themselves with their axes perpendicular to the axes of rotation would result in a polarized state of the kind contemplated. The rotation of the sphere would then give rise to a magnetic field.

In order to estimate the order of magnitude of an effect of this kind necessary to account for the earth's field, let us calculate the radial separation* of the elements of a doublet, which is necessary in order to account for the field, assuming that each atom of the rotating sphere takes part. If the radial separation comes out as only a fraction of the diameter of an atom, the meaning will of course be, that it is only necessary for the axes of the doublets to turn on the average through a small angle in favour of the radial direction. To save complication of the expressions, we shall deal with the case of a sphere composed of one elementary substance.

If h is the radial doublet separation referred to, n the number of molecules per c.c., and e the electronic charge, the magnetic field at the surface and at the equator is $H = 1{\cdot}75\, neh\omega a$ (see appendix, Problem 4). The field which would act on a compass-needle moving with the earth is found as in the case of the uniformly charged sphere, and is

$$H_1 = 1{\cdot}75\, neh\omega a - 4\pi\omega a F,$$

where F is the electric polarization at the equator, and is given by $4\pi F = 2{\cdot}2\, \pi neh$ (see appendix, Problem 5). Thus the counteracting field brought about by the motion of the needle is again the main factor in the expression, as in the case of the last problem. Taking the case of a silver sphere, containing $0{\cdot}8 \times 10^{23}$ molecules per c.c., we find that, in order to account for a field equal to that of the earth, we must have h equal to 2×10^{-8} cm. Now this is just of the order of the diameter of an atom, which means that it would be necessary for all the doublets to point with their axes completely perpendicular to the axis of rotation. It may be mentioned that the order of magnitude of the quantity h is not materially altered if we take a copper sphere, for example.

The fact that h comes out of the order of the diameter of an atom, is a fact sufficiently tempting, and suggestive, to encourage us to try to get over the difficulties associated with the theory, but there seems little hope of being able to account for the perfect radial distribution required. Considerations of a statistical nature would suggest, that, if ϕ is the angle made by the axis of a doublet with the radial direction, the mean value of $\cos\phi$ is of the order of the ratio of the potential energy of a doublet in the radial configuration, to the kinetic energy of a gas molecule at the same temperature. All ordinary views as to the means by which the potential energy of the configuration might arise, however, lead to a value of $\cos\phi$ of far too small an order of magnitude. When once a set of doublets got into radial configuration, they would have a fairly strong tendency to retain that state, just as the molecular magnets which constitute a magnetized ring of iron tend to hold themselves in the magnetized configuration; though it must be admitted that with our knowledge of the temperature conditions inside the earth, and the absence of our knowlege of any example of permanent electrostatic retentiveness, do not lend support to the hypothesis.

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* By the radial direction we here mean the direction perpendicular to the axis of rotation.

The form of the theory is such as to make the field at the equator proportional to ωa, which would mean that, apart from temperature considerations, it would be quite easy to produce a field equivalent to that of the earth, by rapidly rotating a sphere in the laboratory.

It may be shown from the expression on page 93, that the surface electric field required by the theory is about 10^6 E.S.U., and the difficulties in this respect would have to be overcome as in the last problem, by imagining a surface distribution such as to just annul the electrostatic field.

The possibility of an explanation of the field as arising from a directive orientation of the molecular magnets which represent the atoms.

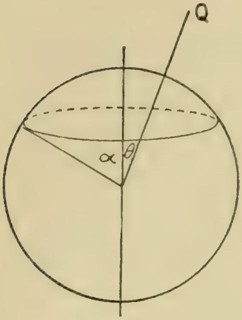
Consider a sphere in which there are n atoms per c.c. Let m be the moment of the atomic magnet to which the resultant atomic whirl in the atom at large distances is equivalent. Let ϕ be the angle made by the axis of the atomic magnet with the axis of the earth's rotation, and let j be the average value of $\cos\phi$ for all the atoms in a cubic centimetre. Considering first a case where j is simply a function of ω, we find, for the horizontal magnetic field due to the sphere $H=\frac{4}{3}\pi\frac{a^3}{r^3}jnm\sin\theta$ (see appendix, Problem 6). The field is thus independent of the size of the sphere, depending only on the angular velocity, so that by rotating spheres in the laboratory we could obtain fields enormously greater than that of the earth.

j may be a function of the velocity, and of the acceleration of the element of matter to which it refers, but no terms involving the velocity only can be of importance, as the effect resulting from the translatory motion of the earth, would, owing to the obliquity of the ecliptic, result in a large diurnal variation. Again, it is easy to see that terms in the expression of j proportional to the radial acceleration f would make the field at the surface come out proportional to ω^2a, which would again result in a field readily detectable on a small sphere rotating in the laboratory, so that it would seem that there are very great difficulties in imagining the directive orientation of the molecular magnets to arise as a direct result of the earth's rotation, and any other explanation of the orientation is virtually equivalent to an assumption of permanent magnetization.

In conclusion, it may be remarked that the difficulties attending the explanation of the earth's field as arising from currents brought about by its rotation are decidedly less than those attending the explanation of the effect as due to the other causes we have discussed; and though want of coincidence of the geographical and magnetic axes is not involved as an obvious necessity, the difficulties in this respect seem less insurmountable than in the case of the rotation of the charged spheres. If, for instance, in the complete elucidation of the causes of these currents, it were found that the effect of the earth's orbital motion, and of its radial motion towards the sun, were to cause the currents of which we have spoken to circulate, not about the geographical axis, but rather about an axis which rotates about the geographical axis with a period of one day, we should have an explanation of the want of coincidence between the two axes, consistent with the permanent position of the magnetic axis with respect to the earth as a whole. A slight difference in the periods, amounting to a loss of one complete revolution in 400 years, would explain the secular variation, and smaller terms in the expression of the difference of periods would result in the annual variation, &c.

APPENDIX.

(1) *The magnetic field due to a sphere of radius* a *rotating with angular velocity* ω *and charged to a surface density* s.



The current due to the rotation of a zone of width $ad\alpha$ subtending an angle α with the axis of rotation at the centre of the sphere, is

$$\omega as\,.\,a\sin\alpha\,.\,d\alpha.$$

The magnetic potential due to such a current at a point Q whose polar coordinates are $r\,.\,\theta$, is (see Maxwell's 'Electricity and Magnetism,' vol. ii. p. 333)

$$\delta\Omega = 2\pi sa^2\omega\sin^3\alpha\,.\,d\alpha\sum_{n=1}^{n=\infty}\frac{1}{n+1}\,.\,\frac{a^{n+1}}{r^{n+1}}\mathrm{P}_n'(\alpha)\,.\,\mathrm{P}_n(\theta),$$

where P_n stands for the ordinary spherical harmonic of degree n.

The potential due to the rotating sphere is

$$\Omega = 2\pi\omega s\sum_{n=1}^{n=\infty}\frac{a_{n+3}}{(n+1)r^{n+1}}\,.\,\mathrm{P}_n(\theta)\int_0^\pi \mathrm{P}_n'(\alpha)\sin^3\alpha\,.\,d\alpha.$$

Writing the integral as I_n, we readily find by the application of the ordinary processes of spherical harmonics, $\mathrm{I}_n=0$ except when $n=1$, in which case $\mathrm{I}_n=\frac{4}{3}$.

$$\therefore\ \Omega = \frac{4}{3}\pi s\omega\frac{a^4}{r^2}\cos\theta.$$

The horizontal component of the field is

$$-\frac{\partial\Omega}{r\partial\theta} = \frac{4}{3}\pi s\frac{a^4}{r^3}\omega\sin\theta.$$

At the surface of the sphere and on the equator, we have $\mathrm{H}=\frac{4}{3}\pi sa\omega$, or if V represents the potential of the sphere, we have

$$\mathrm{H} = \frac{\mathrm{V}}{3}\omega.$$

(2) *The magnetic field due to a rotating sphere of radius a in which currents circulate round the axis, the current density σ being proportional to the distance from the axis of rotation and to the square of the angular velocity.*

Consider any spherical shell of radius y, and thickness dy. The current density in this shell may be written in the form

$$\sigma=\sigma_0\omega^2 y \sin\alpha.$$

The current in the element $yd\alpha\,.\,dy$ is

$$\sigma_0\omega^2 y^2 \sin\alpha\,.\,d\alpha\,.\,dy,$$

so that the problem of finding the magnetic potential $\Delta\Omega$, due to the shell, is the same as that worked out in problem (1), and we have

$$\Delta\Omega=\frac{4}{3}\pi\sigma_0\omega^2\frac{y^4}{r^2}\cos\theta\,.\,dy.$$

The magnetic potential Ω, due to the whole solid sphere, is

$$\Omega=\frac{4}{3}\pi\sigma_0\frac{\omega^2}{r^2}\cos\theta\int_0^a y^4\,dy=\frac{4}{15}\pi\sigma_0\frac{\omega^2}{r^2}a^5\cos\theta.$$

The horizontal component H of the field is

$$-\frac{\partial\Omega}{r\partial\theta}=\frac{4}{15}\pi\sigma_0\frac{\omega^2}{r^3}\,.\,a^5\sin\theta.$$

At the equator on the surface of the sphere we have

$$\mathrm{H}=\frac{4}{15}\pi\sigma_0\omega^2 a^2.$$

(3) *The magnetic field due to a sphere of radius a, rotating with angular velocity ω, the current density being merely a function of ω.*

If $\sigma=\mathrm{F}(\omega)$, the current in the ring of cross-section $yd\alpha\,.\,dy$, lying on the sphere of radius y, is $y\mathrm{F}(\omega)d\alpha\,.\,dy$.

The magnetic potential due to this ring of current at the point $r\,.\,\theta$ is

$$\delta\Omega=2\pi y\,dy\,\mathrm{F}(\omega)\sin^2\alpha\sum_{n=1}^{n=\infty}\frac{1}{n+1}\cdot\frac{y^{n+1}}{r^{n+1}}\,.\,\mathrm{P}_n'(\alpha)\,.\,\mathrm{P}_n(\theta)d\alpha.$$

The potential due to the whole shell of thickness dy is

$$\Delta\Omega=2\pi\mathrm{F}(\omega)\sum_{n=1}^{n=\infty}\frac{1}{n+1}\cdot\frac{y^{n+2}}{r^{n+1}}\,.\,\mathrm{P}_n(\theta)\,dy\int_0^\pi \mathrm{P}_n'(\alpha)\sin^2\alpha\,.\,d\alpha.$$

Writing I_n for the integral, we find for the potential due to the whole sphere of radius a,

$$\Omega = 2\pi F(\omega) \sum_{n=1}^{n=\infty} \frac{I_n}{(n+1)(n+3)} \cdot P_n(\theta) \frac{a^{n+3}}{r^{n+1}}.$$

After some rather cumbersome work involving the usual processes, we obtain I_n, and finally Ω, which, expressed to two terms of a series, is

$$\Omega = F(\omega) \left\{ 0{\cdot}194 P_1(\theta) \frac{a^4}{r^2} + 0{\cdot}123 P_3(\theta) \frac{a^6}{r^4} + \ldots \right\}.$$

The horizontal field is

$$-\frac{\partial\Omega}{r\partial\theta} = -F(\omega) \left\{ 0{\cdot}194 \frac{a^4}{r^3} \cdot \frac{dP_1(\theta)}{d\theta} + 0{\cdot}041 \frac{a^6}{r^5} \cdot \frac{dP_3(\theta)}{d\theta} + \ldots \right\}.$$

At the equator we have

$$H \propto aF(\omega).$$

(4) *The magnetic field due to the rotation of a sphere in which each atom is arranged with its doublet axis perpendicular to the axis of rotation.*

Consider any ring perpendicular to the axis, lying on the sphere of radius y. Let us find the magnetic field due to a set of doublets rotating with this ring, their axes being all perpendicular to the axis of rotation. Let h be the doublet separation, N the number of charge elements per centimetre on the ring containing the inner members of the doublets. Let $x = y \sin \alpha$ be the radius of the inner ring, and $\delta\Omega$ the magnetic potential at the point $r \,.\, \theta$ due to the rotation of the inner ring.

Then

$$\delta\Omega = 2\pi N e y \sin \alpha \,.\, \omega \sin^2 \alpha \sum_{n=1}^{n=\infty} \frac{1}{n+1} \cdot \frac{y^{n+1}}{r^{n+1}} \cdot P_n'(\alpha) \,.\, P_n(\theta).$$

Let dashed letters refer to the outer ring, so that

$$\delta\Omega' = 2\pi N' e y' \sin \alpha' \,.\, \omega \sin^2 (\alpha + d\alpha) \sum_{n=1}^{n=\infty} \frac{1}{n+1} \cdot \frac{(y+dy)^{n+1}}{r^{n+1}} \times P_n'(\alpha + d\alpha) \,.\, P_n(\theta).$$

where $y + dy$ and $\alpha + d\alpha$ are written in places for y' and α' respectively. If $\Delta\Omega$ is the magnetic potential due to the rotation of these two rings, we have, since

$$N' y' \sin \alpha' = N y \sin \alpha,$$

$$\Delta\Omega = 2\pi N e h a \omega \sin \alpha \frac{\partial}{\partial r} \left\{ \sin^2 \alpha \sum_{n=1}^{n=\infty} \frac{1}{n+1} \cdot \frac{y^{n+1}}{r^{n+1}} \cdot P_n'(\alpha) \,.\, P_n(\theta) \right\}$$

Now we can readily show that

$$\frac{\partial}{\partial x} = \sin\alpha \,.\, \frac{\partial}{\partial y} + \frac{\cos\alpha}{y} \,.\, \frac{\partial}{\partial \alpha}.$$

Carrying out this operation of differentiation we have

$$\Delta\Omega = 2\pi \mathrm{N} eh\omega \sum_{n=1}^{n=\infty} \left\{ \frac{y^{n+1}}{r^{n+1}} \,.\, \mathrm{P}_n(\theta) \,.\, \mathrm{P}_n'(\alpha) \,.\, \sin^4\alpha \right.$$

$$\left. + \frac{\sin\alpha \,.\, \cos\alpha}{n+1} \,.\, \frac{y^{n+1}}{r^{n+1}} \,.\, \mathrm{P}_n(\theta) \frac{d}{d\alpha} \left[\sin^2\alpha \,.\, \mathrm{P}_n'(\alpha) \right] \right\}.$$

It readily follows that if n is the number of doublets per c.c., the magnetic potential due to the ring of cross-section $y d\alpha \,.\, dy$ is obtained by replacing N in the above expression by $ny\, d\alpha\, dy$. Making this substitution, and then integrating with respect to α from 0 to π, and with respect to y from 0 to a, we obtain, without much difficulty, the magnetic potential due to the sphere of radius a in the form

$$\Omega = 2\pi neh\omega \sum_{n=1}^{n=\infty} \frac{a^{n+3}}{r^{n+1}} \,.\, \mathrm{P}_n(\theta) \int_{-1}^{+1} \mu \sqrt{1-\mu^2} \,.\, \mathrm{P}_n(\mu) d\mu,$$

where $\mu = \cos\alpha$.

After some rather laborious work the integral becomes evaluated as a function of n. We need only concern ourselves with the first three terms, which lead to

$$\mathrm{H} = -\frac{1}{r}\frac{\partial\Omega}{\partial\theta} = \frac{\pi^2 neh\omega}{4} \left\{ \frac{a^4}{r^3} \sin\theta + \left[0{\cdot}46 \sin 3\theta + 0{\cdot}09 \sin\theta \right] \frac{a^6}{r^5} \right.$$

$$\left. + \left[0{\cdot}112 \sin 5\theta + 0{\cdot}04 \sin 3\theta + 0{\cdot}01 \sin\theta \right] \frac{a^8}{r^7} + \ldots \right\}.$$

At the equator, and on the surface, H amounts to $1{\cdot}75\, neh\omega a$.

(5) *The electrostatic field due to the sphere considered in the last problem.*

In the notation of the last problem the electrostatic potential due to the charge elements of the same kind in the ring of radius $x = y \sin\alpha$ is, at the point $r \,.\, \theta$,

$$\delta \mathrm{V} = 2\pi \mathrm{N} ey \sin\alpha \sum_{n=1}^{n=\infty} \frac{y^n}{r^{n+1}} \,.\, \mathrm{P}_n(\alpha) \mathrm{P}_n(\theta).$$

The electrostatic potential due to the ring of doublets is

$$\Delta \mathrm{V} = 2\pi h \mathrm{N} e y \sin \alpha \frac{\partial}{\partial x} \sum_{n=1}^{n=\infty} \frac{y^n}{r^{n+1}} \,.\, \mathrm{P}_n(\alpha) \,.\, \mathrm{P}_n(\theta).$$

On replacing N by $ny\,d\alpha\,dy$ in order to obtain the potential due to the ring of cross-section $y\,d\alpha\,dy$ we obtain, on integrating from $\alpha=0$ to $\alpha=\pi$ and from $y=0$ to $y=a$, the potential due to the whole sphere, in the form

$$\mathrm{V} = 2\pi neh \sum_{n=1}^{n=\infty} \frac{1}{n+1} \,.\, \frac{a^{n+1}}{r^{n+1}} \,.\, \mathrm{P}_n(\theta) \{ n\mathrm{I}_n + \mathrm{I}_n' \},$$

where

$$\mathrm{I}_n = \int_0^\pi \sin^2 \alpha \,.\, \mathrm{P}_n(\alpha) d\alpha, \quad \mathrm{I}_n' = \int_0^\pi \sin \alpha \,.\, \cos \alpha \,.\, \frac{\partial}{\partial \alpha} \,.\, \mathrm{P}_n(\alpha) d\alpha.$$

On evaluating these integrals we obtain, for the polarization F at the equator and on the surface,

$$4\pi \mathrm{F} = -\frac{\partial \mathrm{V}}{a \partial \theta} = 2 \cdot 2\pi neh.$$

(6) *The magnetic field due to a sphere in which the axes of the molecular magnets are orientated in favour of the direction of the axis of rotation.*

In terms of the notation on page 94 we find for the moment per c.c.

$$\mathrm{M} = jnm.$$

This corresponds to a sphere magnetized parallel to the axis of rotation, and to an intensity jnm. The case is thus one of a uniformly magnetized sphere, and the magnetic potential at the point $r \,.\, \theta$ is

$$\Omega = \frac{4}{3} \pi \frac{a^3}{r^2} jnm \cos \theta.$$

Thus

$$\mathrm{H} = \frac{4}{3} \pi \frac{a^3}{r^3} jnm \sin \theta.$$

Physical Laboratory,
The University of Sheffield.
March 13, 1912.

VII. *The Kinetic Properties of a Molecule in a Substance.*

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The Minimum Velocity of a Molecule.

IT is usually stated as an assumption that the kinetic energy of a molecule in a liquid is the same as that in a gas at the same temperature. It is possible to obtain definite information on this point, from which it will appear that this loose statement must be considerably modified. This point has already been investigated in a previous paper †. Since the result obtained forms the foundation of the formulæ deduced in this paper, the investigation will in part be repeated.

Suppose that a thermometer is placed in a perfect gas. It will assume the temperature of the gas, through being bombarded by the gas molecules. From experience we know that if the gas is allowed to expand without doing external work, the temperature of the thermometer is not altered, showing that the temperature it indicates is independent of the number of molecules impinging per second per cm.^{2} of its surface. Let us consider the effect of the attraction of the material of the bulb on the molecules of the gas. When a molecule gets into the zone of attraction of the bulb its velocity is increased, and each molecule thus impinges on the bulb with a greater velocity than it possesses when not under the influence of an external force. Now suppose the bulb covered with a material which exerts a much more powerful attraction on the surrounding gas molecules than the material of the bulb. Each molecule now impinges on the bulb with a much greater velocity than before. But we know from experience that the temperature indicated by a thermometer is independent of the material of the bulb. It appears, therefore, that the temperature indicated by a thermometer placed in a gas is regulated by the velocity of the molecules when not under the influence of an external force.

Suppose the thermometer is placed in a liquid. The temperature of the liquid and thermometer are equalized, as before, by the molecules of the liquid bombarding the bulb of the thermometer. Now there must exist a large number of points in a liquid, which like the molecules are in motion, at which the forces of the surrounding molecules neutralize one another. It follows from the above result that the thermometer indicates a temperature corresponding to the velocity a molecule has when passing through one of these points. This velocity is equal to the velocity the molecule has in the gaseous state at the same temperature.

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* Communicated by the Author.

† Proc. Camb. Phil. Soc. vol. xvi. pt. vi. pp. 540–559. This paper deals with the properties of the different internal energies into which the internal energy of a substance can be divided, and the nature of the undetermined function in the law of molecular attraction.

The effect of molecular attraction is to make the molecules in a mass of matter approach one another on collision with a greater velocity than they would have if they did not possess this property. The average velocity of a molecule may thus be much larger than the minimum velocity which corresponds to its temperature.

The Average Velocity of a Molecule.

Van der Waals, in deducing his equation of state, assumes that the velocity of the molecules in a substance is not influenced by their attraction upon one another. But it can be easily shown that this assumption cannot be even approximately true. The effect the molecular attraction has on the velocity and shape of path of a molecule cannot be exactly calculated, owing to mathematical difficulties, and a want of knowledge of the correct form of the law of molecular attraction. But numbers can be obtained which show that the average velocity in a liquid is several times that corresponding to the temperature of the substance, which is the minimum velocity.

Suppose that the volume of a gram of liquid at a low temperature in contact with its saturated vapour changes by dv. The energy spent in overcoming the attraction between the molecules is therefore $\frac{dL}{dv}$, where L denotes the heat of evaporation of the liquid. The distance between two molecules is changed by $\left(\frac{dv}{Nv}\right)^{1/3}$ during the process, where N denotes the number of molecules per c.c. of the liquid; and the rate of expenditure of energy per unit distance per molecule is therefore

$$\frac{dL}{(dv)^{4/3}}\,\frac{1}{N^{2/3}v^{2/3}}, \quad \text{or} \quad -\frac{dL}{(d\rho)^{4/3}}\cdot\rho^{8/3}m_a^{2/3},$$

since $Nm_a=\rho$ and $v=\frac{1}{\rho}$, where ρ denotes the density and

m_a the absolute molecular weight of the liquid. We may assume, without any serious error, that on the average the expenditure of energy of a molecule against the attraction of the surrounding molecules during its motion of translation is proportional to the distance traversed, and per unit distance is equal to the above value. Therefore, when a molecule traverses a distance equal to half the distance of separation of the molecules in the liquid (which permits the molecules to have a diameter equal to half their distance of separation), it may on the average lose or gain in energy an amount equal to $\frac{dL}{(d\rho)^{4/3}} \cdot \frac{\rho^{7/3} m_a}{2}$, or undergo a change in velocity equal to $\left(\frac{dL}{(d\rho)^{4/3}} \rho^{7/3}\right)^{1/2}$. In the case of ether at 273° abs. this change in velocity amounts to $1{\cdot}39 \times 10^5$ cm./sec., using the internal heat determination of Mills*. The minimum velocity of a molecule, which corresponds to that of a molecule in the gaseous state at the same temperature, is equal to $3{\cdot}03 \times 10^4$ cm./sec. We see, therefore, that the average velocity of a molecule in a liquid may be several times that corresponding to its temperature. The same result will be obtained in a different way in a subsequent paper.

The Pressure exerted by the Molecules.

According to the kinetic theory of gases, the pressure exerted by a gas in a closed vessel upon its walls is due to the change in momentum the molecules, which are supposed to be in rapid motion, undergo during collision with the walls of the vessel. Now it will be easily seen that the attraction the walls of the vessel exert on a molecule will not affect the magnitude of the change of momentum during collision. The pressure exerted by a molecule will therefore depend only on its minimum velocity—that is, the velocity it possesses when not under the action of any external force—and the number of times it collides per second with the wall of the vessel. Suppose a molecule collides with the wall of the vessel n_a times per second. The pressure it exerts is then equal to n_aA dynes, where A is a constant which depends only on the nature of the molecule and its temperature.

The constant A can easily be deduced from the kinetic theory of gases. Consider a perfect gas in which there are N molecules per c.c., each of which has a velocity v. Since the direction of motion of a molecule may lie in any direction, we may suppose (as is usually done) that the molecules consist of three sets moving at right angles to one another. Therefore, if n_2 denotes the number of molecules that cross per second a plane 1 cm.^{2} in area, which is at right angles to the motion of the molecules in a set, we have

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* Journ. Phys. Chem. vol. viii. p. 405 (1904).

$$n_2 = \frac{Nv}{3}, \quad \text{or} \quad n_2 = \frac{\rho v}{3m_a},$$

since $Nm_a = \rho$, where m_a is the absolute mass of a molecule and ρ the density of the gas. Now the equation of state of a perfect gas is

$$p = \frac{RT\rho}{m},$$

where p is its pressure in dynes and T its temperature, m is the mass of a molecule relative to hydrogen, and R is a constant whose value is $8{\cdot}26 \times 10^7$. But we also have

$$p = n_2 A,$$

and hence

$$\frac{\rho v A}{m_a 3} = \frac{8{\cdot}26 \times 10^7 \rho T}{m}, \quad \text{or} \quad A = 2{\cdot}478 \times 10^8 T \frac{m_a}{mv}.$$

From the kinetic theory of gases, we have

$$v^2 = \frac{3p}{\rho} = \frac{3RT}{m},$$

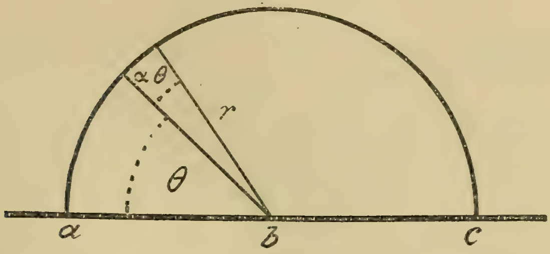
and thus

$$\begin{aligned} A = (3R)^{1/2} \frac{m_a}{m} \sqrt{Tm} &= (3 \times 8{\cdot}26 \times 10^7)^{1/2} \frac{m_a}{m} \sqrt{Tm} \\ &= 2{\cdot}534 \times 10^{-20} \sqrt{Tm}, \end{aligned}$$

on substituting $1{\cdot}61 \times 10^{-24}$ for $\frac{m_a}{m}$, the absolute mass of the hydrogen atom determined by Rutherford from experiments on the α particle.

It follows from the above that if n_3 molecules cross a plane 1 cm.^{2} in area per second at right angles in one direction in a substance of any density, the pressure these molecules produce is $n_3 A$. But since the molecules in a substance cross the plane in all directions, it will be necessary to investigate the pressure they produce in terms of the total number n passing through the plane from one side to the other. Take a point b on a plane abc (fig. 1), and draw a sphere of radius r around it, and let the angle a line through b makes

Fig. 1.



with the plane be denoted by θ. Suppose s molecules impinge per cm.^{2} per second at right angles on the surface of the sphere. The number impinging on a circular belt of breadth $r\,.\,d\theta$ and radius $r\cos\theta$ is therefore $2\pi r^2 s\cos\theta\,.\,d\theta$. The pressure exerted by a molecule on impinging on the plane abc at an angle θ is proportional to its component velocity at right angles to the plane, and thus equal to $A\dfrac{v\sin\theta}{v}$ or $A\sin\theta$. Hence the molecules in the solid angle π impinging on the point b exert the pressure

$$\int_0^{\frac{\pi}{2}} 2\pi r^2 sA\sin\theta\,.\cos\theta\,.\,d\theta=\pi r^2 sA.$$

If u denote the number of molecules impinging on the point b we have

$$u=2\pi r^2 s,$$

and the pressure exerted by the molecules may be written $\frac{u}{2}A$. Hence if n denote the total number of molecules passing through 1 cm.^{2} per second, the pressure they exert is

$$\frac{n}{2}A=n1{\cdot}27\times10^{-20}\sqrt{Tm}.$$

The pressure under consideration is balanced by the sum of the external pressure and the negative pressure due to the attraction of the molecules upon one another, called the intrinsic pressure. Hence, if these two quantities are denoted by p and P_n respectively, we have

$$\frac{n}{2}A = p + P_n,$$

or $$n\, 1{\cdot}27 \times 10^{-20} \sqrt{Tm} = p + P_n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This is the equation of state of a substance involving the quantities P_n, p, T, and n.

If we suppose that the motion of the molecules takes place parallel to three straight lines at right angles to one another, and an equal number move parallel to each line, the number that cross in one direction a plane 1 cm.^{2} in area parallel to one of the directions is given by

$$nA = P_n + p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It will be of interest to obtain numerical values of n for a liquid at low temperatures, the intrinsic pressure being then large in comparison with the external pressure. Approximate values for the intrinsic pressure can be obtained from the equation

$$P_n = L_1 \rho,$$

where L_1 denotes the energy necessary to separate the molecules of a gram of substance by an infinite distance from one another ; when the density of the vapour is small in comparison with that of the liquid, L_1 is the internal heat of evaporation. This equation is deduced on the supposition that matter is evenly distributed in space, *i. e.*, does not consist of molecules. The values of P_n can also be obtained by means of the equation

$$P_n = -\frac{T\alpha}{\beta},$$

where α denotes the coefficient of expansion with rise of temperature, and β the coefficient of compression at constant temperature. In deducing this equation, the change in internal energy of a molecule with a change in the density of the substance was assumed to be zero. Both equations give approximately the same result *. Using the latter equation, the values of n at different temperatures given by equation (2) have been calculated for four liquids, and are given in Table I., which also contains the values of n calculated on the supposition that each substance behaves as a perfect gas. The values of n in the latter case are given by $\frac{\rho v}{m_a 3}$. The data were obtained from Landolt and Börnstein's tables. It will be seen that the values of n in the former case are much larger than in the latter.

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* *Loc. cit.*

TABLE I.

Ether, $C_4H_{10}O$.				Ethyl Chloride, C_2H_5Cl.			
t.	$T\frac{\alpha}{\beta}$.	$n\,10^{-26}$.	$n\,10^{-25}$ (as perf. gas).	t.	$T\frac{\alpha}{\beta}$.	$n\,10^{-26}$.	$n\,10^{-25}$ (as perf. gas).
13·5	2669	7·1	6·24	11	3383	9·9	
78·5	1812	4·4	6·16	99	2042	6·1	
Pentane, C_5H_{12}.				Chloroform, $CHCl_3$.			
0	1747	4·9	5·23	0	2991	6·5	6·30
60	1260	3·2	5·68	60	2726	5·4	6·50

This result is due to two causes. One of them is that the actual volume occupied by the molecules is comparable with that occupied by the matter as a whole. Consequently the molecules have not so much room for motion as if they consisted of points, which increases their frequency of collisions and change of direction of motion, and thus increases the value of n. The other cause is the attraction that exists between the molecules. It has the effect of making two molecules about to collide to pass over their distance of separation more quickly than if they exerted no attraction upon one another. The attraction thus has the effect of increasing the average velocity of each molecule and consequently the value of n.

The quantity n can be expressed in terms of more fundamental quantities than those contained in equation (1). In previous papers * I have shown that

$$p = M^2 \left(\frac{\rho}{m}\right)^{7/3} (\Sigma\sqrt{m_1})^2$$

and

$$P_n = K_2 \left(\frac{\rho}{m}\right)^{7/3} (\Sigma\sqrt{m_1})^2,$$

where M^2 and K_2 are quantities which have the same value

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* Phil. Mag. Dec. 1909, p. 903, and May 1910, p. 788, and Oct. 1910, p. 668.

for all substances at corresponding states, and $\Sigma\sqrt{m_1}$ denotes the sum of the square roots of the atomic weights of the atoms of a molecule. These equations are based on the law of molecular attraction:

$$\phi\left(\frac{T}{T_c},\frac{x_c}{z}\right)\cdot\frac{(\Sigma\sqrt{m_1})^2}{z^5},$$

where z is the distance of separation between two molecules and x_c their distance of separation in the critical state. Substituting the above values of p and P_n in equation (1) or (2) we obtain

$$n=\frac{W_1\rho^{7/3}(\Sigma\sqrt{m_1})^2}{T^{1/2}\,m^{17/6}}\quad\ldots\ldots\quad(3)$$

where W_1 is the same for all substances at corresponding states. This equation is perfectly general and therefore also applies to a perfect gas.

Table II.

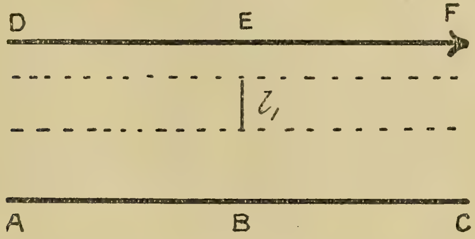
Ether, Liquid. Temp. 311°·7.				Benzene, Liquid. Temp. 374°·4.			
$\frac{T\alpha}{\beta}$.	ρ.	n (Equat. 2).	n (Equat. 3).	$\frac{T\alpha}{\beta}$.	ρ.	n (Equat. 2).	n (Equat. 3).
2366	·6907	$6·18\times10^{26}$	$6·8\times10^{26}$	3807	·7826	$9·73\times10^{26}$	$8·7\times10^{26}$
Ether, Gas. Temp. 311°·7.				Benzene, Gas. Temp. 374°·4.			
	$\frac{\rho_c}{10{,}000}$	n (K. Th. of Gases).	n (Equat. 3).		$\frac{\rho_c}{10{,}000}$.	n (K. Th. of Gases).	n (Equat. 3).
	$2·604\times10^{-5}$	$2·46\times10^{21}$	$2·5\times10^{21}$		$3·045\times10^{-5}$	$3·58\times10^{21}$	$3·52\times10^{21}$

Table II. gives the values of n calculated by equation (2), in the same way as before, for two substances in the liquid state at the temperature $\frac{2T_c}{3}$, and those calculated by equation (3) putting $W_1=7·3\times10^{31}$. The table contains also the values of n corresponding to the temperature $\frac{2T_c}{3}$ and density $\frac{\rho_c}{10{,}000}$, when the substances are in the gaseous state, calculated from the kinetic theory of gases, and the values calculated from equation (3) putting W_1 equal to $5{\cdot}75 \times 10^{36}$. A fair agreement between the two sets of values is obtained in each case.

A General Formula for the Coefficient of Viscosity.

The results obtained in this paper enable us to obtain a formula for the coefficient of viscosity for matter of any density. Let ABC, DEF in fig. 2 represent a mass of matter in which the molecules are more or less bodily moving, in planes parallel to DEF, in the direction from D to F. Let the molecules in the plane DEF have unit velocity and those in the plane ABC be at rest, and the velocity change gradually as we pass from the plane DEF to the plane ABC. If the planes are separated by unit distance, the force necessary to apply to the plane DEF per cm.^{2} to maintain unit velocity is the coefficient of viscosity. Consider a molecule moving along BE at right angles to the planes. Let $v_1 m_a$ denote its momentum parallel to DEF at the beginning of the motion, which is taken the same as that of the surrounding matter, and $v_2 m_a$ its momentum when it ceases to absorb momentum parallel to DEF from the surrounding molecules, and let l_1 denote the distance between these two stages. The change of velocity per unit distance as we pass from E to B is equal to unity, and therefore $\frac{v_1 - v_2}{l_1} = 1$. It should be noticed that the molecule does not necessarily retrace its path when it ceases to absorb momentum parallel to DEF. Let us suppose that the molecules move parallel to three directions one of which is at right angles to the plane DEF. Suppose n_1 molecules cross per second from B towards E, through a plane 1 cm.^{2} in area parallel to the plane DEF. There is therefore a gain of momentum per cm.^{2} per sec. equal to $n_1(v_1 m_a - v_2 m_a)$ in the plane parallel to DEF, passing through the end of the

Fig. 2.



molecular path l_1. The viscosity η is equal to this gain of momentum, and hence $\eta = n_1(v_1 m_a - v_2 m) = n_1 l_1 m_a$. Now the value of n_1 is given by the equation $n_1 A = P_n + p$, and the foregoing equation becomes

$$\eta = \frac{l_1 m_a}{A}(P_n + p) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The equation is perfectly general. In the case of a perfect gas $P_n = 0$, $p = \frac{RT\rho}{m}$, and $v^2 = \frac{3RT}{m}$, which reduce the equation to the well-known form $\eta = \frac{1}{3}\rho v l_1$. It is of interest to note that it follows from the above equation that the viscosity of a liquid might in some cases be greatly increased by increasing the external pressure without necessarily producing any appreciable change in density.

Table III. contains the values of l_1, calculated by means of equation (4) for three liquids, using the values of P_n given

Table III.

Substance.	t°.	ρ.	η (Liquid).	L.	l_1 (Liquid).	l_1 (Gas).
Benzene	0	·9001	·009025	100	$7{\cdot}02 \times 10^{-8}$ cm.	$8{\cdot}0 \times 10^{-9}$ cm.
Chloroform	0	1·5264	·00700	62·45	4·14 ,,	9·96 ,,
Methyl-Isobutyrate...	18·12	·8891	·005299	82·5	4·59 ,,	9·1 ,,

by the equation $P_n = L_1\rho$. The table also contains the values of l_1 calculated by means of the equation $\eta = \frac{1}{3}\rho v l_1$, which supposes that the liquid behaves as a perfect gas. It will be seen that the former values are larger than the latter. This can be easily explained if the interaction of the molecules during "collision" is largely due to the field of force surrounding them. The amount a molecule gets deflected when it flies past another molecule in that case depends on the vicinity of other molecules. Thus, if a molecule *a* flies between two molecules *b* and *c* some distance apart, the deflexion of *a* caused by *b* will be smaller than when *c* is absent, the attraction of *b* being partly neutralized by that of *c*. It will be evident therefore that the "radius of the sphere of action of a molecule" in a substance will decrease with its density. The mean free path will therefore not vary inversely as the density over all ranges of densities, but less rapidly with an increase of density when this has reached a certain value. It is very probable that when l_1 ceases to vary inversely as the density of a substance, P_n ceases to be negligible in comparison with p, since the deviation in each case would be caused by the influence of molecular attraction.

The particular density of a gas at which l_1 ceases to vary inversely as the density is therefore of interest. It occurs, according to the equation $\eta=\frac{1}{3}v\rho l$, when the viscosity ceases to be independent of the density. The variation of the viscosity of CO_2 with the density is shown in Table IV.,

TABLE IV.

p (mm. Hg.).	ρ.	η.	p (atmos.).	ρ.	η.
·6	Proportional to pressure.	·0001433	43·1	0·100	·000177
2·4		1498	60·7	·170	189
380		1511	79·3	·590	429
750		1524	111·5	·800	683

which is taken from Weinstein *. It will be seen that the deviations of the viscosity from constancy as the density is increased do not occur abruptly, showing that there is no abrupt change in the field of force surrounding a molecule, as we pass from its centre outwards.

A General Formula for the Coefficient of Conduction of Heat.

A general formula for the coefficient of conduction of heat can be obtained along the same lines as that for the viscosity. The amount of heat that crosses 1 cm.^{2} per second in a substance, when the heat gradient is 1 degree per cm., is usually defined as the conductivity or the coefficient of conduction. Consider a molecule moving in the direction of the flow of heat at the standard temperature gradient. Let its temperature be that of the surrounding molecules at the beginning of the motion, and let l_2 denote the distance in the direction of flow of heat it traverses before its temperature is reduced to that of the surrounding molecules. Let t_1 and t_2 denote the temperatures of the molecule at the beginning and end of its journey. The temperature in each case is that corresponding to the minimum velocity of the molecule.

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* *Thermodynamik und Kinetik der Körper,* i. pp. 325–326.

Then, since the temperature gradient is unity, $\frac{t_1-t_2}{l_2}=1$. It should be noticed that the molecule need not necessarily retrace its path after having traversed the distance l_2. Let us suppose that the motion of the molecules takes place parallel to three directions at right angles to one another, one of which is parallel to the flow of heat. Let n_2 molecules cross per second a plane 1 cm.^{2} in area situated at right angles to the flow of heat and passing through the end of the molecular path l_2. Now when a number of molecules move in the direction of the flow of heat, they not only part with a portion of their original kinetic energy to the surrounding molecules, but also with potential energy due to molecular attraction, &c., since they become more densely congregated. At the same time they gain heat due to the external work done when undergoing compression; this work is done by the surrounding molecules; but an equivalent amount of energy is handed over to them again on equalization of temperature. Thus, in the latter case, there is, on the whole, neither gain nor loss of heat. The amount of heat gained per cm.^{2} per second in the plane in question, when n_2 molecules cross it in the direction of the flow of heat, is therefore $n_2(t_1-t_2)m_a\gamma$ or $n_2l_2m_a\gamma$, where γ is the internal specific heat per gram of substance at constant pressure, and m_a the absolute molecular weight of a molecule. This gain of heat is the conductivity C, or

$$C=l_3m_a\gamma\left(\frac{P_n+p}{A}\right), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

on substituting for n_2 the same value as for n_1 in the previous section.

The mean free path l_1 and l_2 of a molecule relating to viscosity and conduction of heat respectively have very different meanings when the matter is so dense that P_n is comparable in magnitude with p. The quantity l_1 then denotes the distance a molecule traverses till it has a certain component of motion at right angles to its original motion, the minimum kinetic energy remaining unchanged. The quantity l_2 denotes the distance traversed till its minimum kinetic energy has decreased to that of a molecule of the surrounding matter, but during its journey it was receiving energy from changes in the potential energy due to molecular attraction, &c. The ratio of l_1 to l_2 is given by the equation

$$\frac{l_1}{l_2}=\frac{\eta\gamma}{C}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

deduced from equations (4) and (5). Table V. contains the values of this ratio for a few liquids. They are not equal to one another as we should expect. It will also be seen that they are all greater than unity, which means that l_2 is less than l_1 in a liquid. In the case of a gas the opposite holds. It appears, therefore, that when a molecule in a liquid passes from a warmer to a colder part, it spends energy much more rapidly than it acquires through changes in potential energy.

Table V.

	C.	η.	γ.	$\frac{\eta\gamma}{C}$.
Chloroform	$\cdot 0_3 288$	·005876	·2337	4·77
Carbon disulphide ...	$\cdot 0_3 343$	·00381	·243	2·70
Benzene	$\cdot 0_3 333$	·007172	·3319	7·15

It will be observed that l_2 is very small, less than the average distance of separation of the molecules. But this will cease to appear remarkable when it is pointed out that the path l_2 is the straight line joining two definite points on the path of the molecule, which is an undulating curve, and the molecule is therefore often in describing its path separated by a greater distance from its starting-point than the ultimate distance defined as its mean free path l_2.

When there is no change in the potential energy of attraction along the path of a molecule, as occurs in the case of a gas, l_1 may be nearly equal to, or at least proportional to, l_2 for all substances. This is the case with gases, as is well known. In general, then, we ought to write $l_2 = l_1 . \psi(T\rho)$, where $\psi(T\rho)$ is a function of the temperature T and density ρ of the substance, which is greater than unity in the case of a liquid, and in the case of a gas is a constant less than unity equal to about ·7.

A General Formula for the Coefficient of Diffusion.

Suppose a mixture of two substances 3 and 4 is contained between the planes ABC and DEF (fig. 2). Let the ingredients be so distributed that the concentration of the substance 3 is proportional to the distance from the plane ABC, and the concentration of the substance 4 proportional to the distance from the plane DEF. The substance 3 will diffuse towards the plane ABC, and the substance 4 towards the plane DEF. Consider a molecule 3 moving in the direction from E to B at right angles to DEF. Let l_3 denote the distance it traverses till its further direction of motion is equally probable in all directions. It is then in the same state as one of the surrounding molecules. Let N_3 denote the concentration of the molecules 3 at the beginning of the path l_3, and N_3-N_3' that at its end. We have then

$$\left(\frac{N_3-(N_3-N_3')}{l_3}\right)=\frac{N_3'}{l_3}=\frac{dN_3}{dx},$$

where $\frac{dN_3}{dx}$ is the concentration-gradient. Let us suppose, as before, that the motion of the molecules is parallel to three straight lines at right angles to one another, one of which is at right angles to the plane DEF. Suppose n_3 molecules 3 cross (in the direction from E to B) per cm.^{2} a plane situated parallel to DEF and passing through the point where the path l_3 begins. The gain of molecules 3 in the plane at the end of the path l_3 is then $n_3\frac{N_3'}{N_3}$ or $\frac{n_3 l_3}{N_3}\cdot\frac{dN_3}{dx}$[*]. The loss of molecules 4 in the same plane is $\frac{n_4 l_4}{N_4}\cdot\frac{dN_4}{dx}$, where the symbols have corresponding meanings, x being measured in the opposite direction in this case. Therefore, on the whole, there is a gain of

$$\left(\frac{n_3 l_3}{N_3}\cdot\frac{dN_3}{dx}-\frac{n_4 l_4}{N_4}\cdot\frac{dN_4}{dx}\right)$$

molecules, which may be written (M_3-M_4), in the plane. But the space occupied by these molecules is not zero. A portion of the mixture must therefore be transported bodily in the opposite direction to make room for these molecules. Let v_3 and v_4 denote respectively the volumes of occupation of the molecules 3 and 4 in the mixture, *i. e.*, the decrease respectively of the volume of the mixture when a molecule 3 or 4 is removed. It follows that v_3 and v_4 are connected by the equation $N_3v_3+N_4v_4=1$. Let x denote the number of molecules in the portion of the mixture displaced to make room for the molecules (M_3-M_4). The value of x is given by

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[*] Thus the plane receives n molecules 3 per sec. from the other plane and loses itself $n\left(\frac{N_3-N_3'}{N_3}\right)$ molecules, since n may be taken proportional to N_3 for small variations of N_3, and the gain is therefore $n\frac{N_3'}{N_3}$.

$$\frac{xN_3v_3}{N_3+N_4}+\frac{xN_4v_4}{N_3+N_4}=M_3v_3-M_4v_4,$$

or

$$x=\left(\frac{M_3v_3-M_4v_4}{N_3v_3+N_4v_4}\right)(N_3+N_4).$$

The number of molecules 3 gained in the plane in question, which is the diffusion δ_3, is therefore

$$\frac{n_3l_3}{N_3}\cdot\frac{dN_3}{dx}-\frac{xN_3}{N_3+N_4},$$

or

$$\delta_3=\frac{n_3l_3}{N_3}\cdot\frac{dN_3}{dx}-\frac{N_3}{N_3v_3+N_4v_4}(M_3v_3-M_4v_4),$$

and hence

$$\delta_3=\frac{v_4}{N_3v_3+N_4v_4}\left(\frac{N_4n_3l_3}{N_3}\cdot\frac{dN_3}{dx}+\frac{N_3n_4l_4}{N_4}\cdot\frac{dN_4}{dx}\right). \quad . \quad (7)$$

In the case of a gas $v_3=v_4$ and $N_3+N_4=K_a$ constant, which reduces the foregoing equation to the well-known form relating to a perfect gas. But in the case of a liquid v_3 is in general not equal to v_4. A case of special interest is obtained when the concentrations of the two kinds of molecules in a liquid mixture are the same. According to the distribution of the molecules in space in such a case * we should expect that v_3 is equal to v_4. Some other properties of v_3 and v_4 may be noticed in this connexion †.

The rate of diffusion of the molecules 4 in the opposite direction to the molecules 3 is given by equation (7) on interchanging the suffixes 3 and 4. It will be seen that the equations giving the rates of diffusion in the two cases may be written $\delta_3=v_3K$ and $\delta_4=v_4K$, and hence $\frac{\delta_3}{\delta_4}=\frac{v_3}{v_4}$.

The quantities n_3 and n_4 are connected by the equation $n_3A+n_4B=P_n+p$, where P_n is the intrinsic pressure and p the external pressure of the mixture, $A=2\cdot53\times10^{-20}\sqrt{Tm_3}$ and $B=2\cdot53\times10^{-20}\sqrt{Tm_4}$. An equation can be obtained which does not contain these quantities on eliminating them from the above equation and the diffusion equations. The quantity P_n can be obtained in terms of quantities that can be measured by means of the equation $P_n=-\frac{T\alpha}{\beta}$, which

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* Phil. Mag. April 1911, pp. 537–538.

† *Loc. cit.* pp. 546–547.

applies also to mixtures. The resultant equation gives the relation between l_3 and l_4, these being the only quantities in the equation that cannot be directly measured.

If the concentration of one of the ingredients is small in comparison with that of the other, say 3 in comparison with 4, the rate of diffusion of the molecules 3 is according to equation (7) given by

$$\delta_3 = \frac{n_3 l_3}{\mathrm{N}_3} \cdot \frac{d\mathrm{N}_3}{dx} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In the case of a gas $n_3 = \frac{\mathrm{V}_3 \mathrm{N}_3}{3}$, where V_3 is the velocity of translation of a molecule, and the equation assumes the well-known form given in the kinetic theory of gases.

It will be evident from a consideration of the nature of the mean free path l_3 from its definition that it is not necessarily equal to either l_1 or l_2 in the case of a liquid, though this may approximately hold in the case of a gas. We must therefore write, as before, $l_3 = l_1 \, . \, \psi_2(\mathrm{T}_1 \rho)$, where $\psi_2(\mathrm{T}_1 \rho_1)$ in the case of a gas becomes a constant.

The Superior Limit of the Average Velocity of a Molecule in a Substance.

We have seen that the number of molecules crossing a cm.^{2} in a substance increases at a greater rate with the density of the substance than we should expect if it behaves as a perfect gas. If the molecules may be regarded as points, this would be entirely due to an increase in their average velocity due to molecular attraction. The velocity calculated on this supposition is thus the superior limit of the average velocity of a molecule in a substance. Let V_v denote this limiting velocity, ρ the density of the substance, and m_a the absolute molecular weight. The number of molecules n crossing a cm.^{2} per second is then given by

$$n = \mathrm{V}_v \, \frac{\rho}{3m_a},$$

where n is given by equation (1), and hence

$$\mathrm{V}_v = \frac{3m_a}{\rho} \left(\frac{\mathrm{P}_n + p}{\mathrm{A}} \right).$$

The molecular velocity calculated by this equation is usually for a liquid about 10 times its minimum velocity. Since the value of n depends on the finite size of the molecules as well as on the molecular attraction, the average velocity will always be less than V_v.

The above equation may be written

$$V_v = \frac{W_2 \rho^{4/3}}{T^{1/2} m^{11/6}} (2\sqrt{m_1})^2 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

by means of equation (3), where W_2 is the same for all substances at corresponding states. This equation shows how V_v varies with the nature of the substance.

The Velocity of Sound.

Consider a molecule moving in a given direction in a substance. Suppose that after collision with another molecule the latter moves off in the same direction with the same velocity. Suppose this process is repeated when the second molecule undergoes collision, &c. It will be evident on reflexion that the velocity with which this disturbance travels is equal to the superior limit of the average velocity discussed in the previous section. In practice, however, the disturbance in a liquid will be propagated with a much smaller velocity, since two molecules before and after collision do not, as a rule, move in the same straight line. Let us consider the propagation of a disturbance in a liquid at right angles to *abc* in fig. 1 in the direction of the hemisphere. Suppose a molecule moving below *abc* collides with a molecule at *b* which comes from the other side. After the collision the direction of the path of either of the molecules will lie in the hemisphere of radius r. Each direction we will take as equally probable. The mean of the projections of all the paths l lying in the hemisphere on a line at right angles to *abc* is

$$\frac{1}{2\pi r^2 s}\int_0^{\frac{\pi}{2}} 2\pi r \cos\theta \,.\, sr \,.\, d\theta \,.\, l \sin\theta = \frac{l}{2},$$

where s has the same meaning as before. Thus, on the average, the disturbance passes over the distance $\frac{l}{2}$ during the time a molecule passes over the distance l. The velocity of the disturbance is therefore equal to $\frac{V_v}{2}$. But this expression can only give a velocity which agrees roughly with the facts. A disturbance in a liquid consists usually of a wave of compression and rarefaction, which produces first a rise and then a fall of temperature in each portion of liquid over which it passes. This introduces factors of which no account is taken in the above investigation.

The velocity of sound in ether at 0° calculated from the above expression is 1787 metres per second, using the value of P_n given by the equation $P_n = L_1\rho$. The value found by experiment is 1145 metres per sec., which is somewhat smaller than the calculated value. Since V_v, according to equation (9), may be expressed at corresponding states as a multiple of its critical value, a much better agreement with the facts would probably be obtained if we write $V_s = S_1 V_v$, where V_s denotes the velocity of sound and S_1 a quantity which has the same value for all substances at corresponding states. The value S_1 will probably not vary much with the temperature, at a temperature $\frac{T_c}{1 \cdot 7}$ it is from the foregoing equal to ·639.

V_s thus varies with the nature of the liquid in the same way as V_v given by equation (9), which, it should be noticed, holds for matter of any density. If the ether behaved as a perfect gas the velocity of sound would be 302 metres per sec., a very much smaller value than found in practice.

The various formulæ deduced in this paper will be further tested in a paper that will appear in the Proc. of the Camb. Phil. Soc. vol. xvi. part vii.

Cambridge,
March 20, 1912.

VIII. *The Diffusion of Alkali Salt Vapours in Flames.*
By Prof. H. A. Wilson, *F.R.S.*, *F.R.S.C.*[*]

THE experiments described in the following paper were undertaken with the object of finding the coefficients of diffusion of alkali salt vapours in a Bunsen flame. The light emitted by flames containing alkali salt vapours appears to be due to atoms of the alkali metal probably electrically neutral[†] but possibly positively charged. Probably an atom of the metal under the influence of the violent collisions with other atoms loses negative electrons, and so becomes a positive ion. Since, however, many free negative electrons are present in the flame even in the absence of salt, it seems certain that such a positive ion must very soon be neutralized by recombination with electrons. The metal atom therefore will be a positive ion for only a fraction of the time. The process of recombination probably sets up vibrations inside the atom which produce radiation, so that the radiation is emitted by the atoms when neutral, or at any rate when with less than their maximum positive charge. The great facility with which the alkali metals lose electrons makes it possible that at the very high temperature of the flame they may lose more than one negative electron. The velocity of the positive ions of salt vapours in flames has been determined by the writer and by others, so that a knowledge of their coefficients of diffusion enables their charge to be calculated by the well-known method first used by Townsend *.

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[*] Communicated by the Author.

[†] Smithells, Dawson, and Wilson, Phil. Trans. A. vol. cxciii. p. 89 (1899).

The method I have used to get the coefficients of diffusion is very simple. A small bead of salt on a platinum wire is put in the flame and the shape of the region surrounding the bead which emits light is measured. From this and the velocity of the flame gases the coefficient of diffusion can be easily calculated.

The bead of salt evaporates at a very constant rate, and can be regarded as a constant point source of salt vapour in the stream of flame gases. The vapour from the bead diffuses into the surrounding gas, and its concentration at any point can be easily calculated by the theory of diffusion.

Take the origin at the bead and the axis of x along the direction of motion of the flame gases, and let their velocity be v. Consider a small rectangular parallelipiped with sides ∂x, ∂y, ∂z, with its centre at the point x, y, z. Let c denote the amount of salt vapour per c. c. and K its coefficient of diffusion. The amount of vapour entering a side of the parallelipiped of area $\partial y\,\partial z$ is

$$\left\{-\mathrm{K}\left(\frac{dc}{dx}-\frac{1}{2}\partial x\frac{d^2c}{dx^2}\right)+v\left(c-\frac{1}{2}\partial x\frac{dc}{dx}\right)\right\}\partial y\,\partial z;$$

the amount leaving through the opposite side is

$$\left\{-\mathrm{K}\left(\frac{dc}{dx}+\frac{1}{2}\partial x\frac{d^2c}{dx^2}\right)+v\left(c+\frac{1}{2}\partial x\frac{dc}{dx}\right)\right\}\partial y\,\partial z.$$

Hence the rate of increase of the amount inside for these two sides is

$$\left\{\mathrm{K}\frac{d^2c}{dx^2}-v\frac{dc}{dx}\right\}\partial x\,\partial y\,\partial z.$$

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* Phil. Trans. A. vol. cxciii. p. 129 (1900).

For the other two pairs of sides the rate of increase is

$$\mathrm{K}\left(\frac{d^2c}{dy^2}+\frac{d^2c}{dz^2}\right)\partial x\,\partial y\,\partial z.$$

Hence in a steady state we have

$$\mathrm{K}\left(\frac{d^2c}{dx^2}+\frac{d^2c}{dy^2}+\frac{d^2c}{dz^2}\right)-v\frac{dc}{dx}=0. \quad . \quad . \quad . \quad (1)$$

To determine the distribution of the salt vapour round the bead of salt we have to find a solution of this equation satisfying the conditions that at the origin there is a constant source of salt vapour, and that at very great distances from the origin the concentration is very small. Such a solution of (1) is

$$c=\frac{\mathrm{A}\epsilon^{\alpha(x-r)}}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $r=\sqrt{x^2+y^2+z^2}$, and A and α are constants *.

If this is put in (1) we find that $\alpha=v/2\mathrm{K}$. When x and r are very small (2) gives $c=\mathrm{A}/r$; so that if q is the amount of salt evaporating per second we have

$$-\mathrm{K}\frac{dc}{dr}4\pi r^2=4\pi\mathrm{AK}=q;$$

or

$$\mathrm{A}=q/4\pi\mathrm{K}.$$

Hence

$$c=\frac{q}{4\pi\mathrm{K}r}\,\epsilon^{\frac{v}{2\mathrm{K}}(x-r)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Owing to the disturbance of the flow of the gases by the bead this equation will not be exactly true close to the bead, but it will hold accurately at distances large compared with the radius of the bead. The shape of the region round the bead which emits visible light will be bounded by a surface over which c has a constant small value, say c'. If therefore we observe the values of x and r at two points on this surface, we have

$$c'=\frac{q}{4\pi\mathrm{K}r_1}\,\epsilon^{\frac{v}{2\mathrm{K}}(x_1-r_1)},$$

$$c'=\frac{q}{4\pi\mathrm{K}r_2}\,\epsilon^{\frac{v}{2\mathrm{K}}(x_2-r_2)},$$

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* H. A. Wilson, Proc. Camb. Phil. Soc. vol. xii. pt. 5 (1904).

which give

$$K = \frac{v(x_2 - x_1 - r_1 + r_2)}{2 \log r_2/r_1}.$$

The shape of the region emitting light is rather like an ellipsoid of revolution with the long axis vertical and the bead at the lower focus. I have found it convenient in practice to observe the greatest horizontal diameter and the corresponding value of r. To find the maximum value of the diameter we differentiate

$$c' = \frac{q}{4\pi K r} \epsilon^{\frac{v}{2K}(x-r)},$$

and put $dy/dx = 0$ and $z = 0$, which gives

$$K = \frac{v}{2} \frac{r_m}{x_m} (r_m - x_m),$$

where r_m and x_m denote the values of r and x at a point where the diameter is a maximum.

A steady flame was obtained by passing the coal-gas and air from an ordinary Bunsen burner through a box containing baffle-plates to thoroughly mix them. The mixed gases were burnt from a vertical brass tube about half an inch in diameter. A brass tube about $\frac{7}{8}$ inch in diameter and 3 inches long was supported so as to be concentric with the first tube, and the top of this second tube was about one inch higher than the top of the other. The inner cone of the flame was just below the top of the outer tube. This arrangement gave a very steady flame the diameter of which was nearly constant for 3 inches above the burner. The outer tube prevented the wobbling of the flame. A small bead of the salt to be investigated was supported on a platinum wire about 1 cm. above the tip of the inner cone. Two fine platinum wires supported on adjustable stands were adjusted so that their ends just touched the surface of the region emitting visible light at opposite ends of a horizontal diameter of its widest part. The distance from the bead to the end of either wire was measured, and also the distance between the ends of the two wires. These distances are r_m and $2y_m$. We have then $x_m = \sqrt{r_m^2 - y_m^2}$.

To find the coefficient of diffusion of the salt vapour we require also to know the velocity of the flame gases. Small luminous particles moving up the flame could be seen to travel along parallel vertical straight lines for several inches above the burner. The velocity was found by means of a bead of sodium sulphate which was supported on a wire attached to one prong of a vibrating tuning-fork. The fork also carried two small screens between which the flame could be seen once in each vibration of the fork. The salt vapour from the vibrating bead when observed through the screens had a wavy outline, and the wave-length was measured. The wave-length multiplied by the number of vibrations per sec. gives the upward velocity of the flame. In this way the velocity was found to be about 200 cm. per sec.

The experiments do not admit of much accuracy because it is difficult to set the platinum wires on the rather hazy boundary of the region emitting light. After some practice, however, independent values found for K did not differ by more than about 10 per cent.

In addition to the region emitting light which surrounds the bead, there is a separate region which forms a sheath covering the outside of the flame. This extends from the top of the flame down to a few centims. above the bead. This outer sheath obscures the upper part of the inner region and makes the observations more difficult. Very often the inner region is not the same colour as the sheath. The cæsium and lithium salts available contained some sodium, and the bright coloration due to it made it difficult to set the wires on the edge of the coloration. In the case of the lithium salt the red colour was outside the sodium yellow, so that it did not matter much, but the cæsium coloration was badly obscured.

The following table gives the values found in centims. for the distance from the bead to a point on the widest part of the inner region emitting light (r_m) and the width of the widest part ($2y_m$). Each number is the mean of several determinations.

	r_m.	$2y_m$.	K.
Lithium	2·4	1·6	14·5
Sodium	2·0	1·3	11·5
Potassium	2·0	0·85	4·7
Rubidium	1·9	0·80	4·4
Cæsium	1·9	0·80	4·4

It appears that cæsium, rubidium, and potassium salt vapours diffuse at nearly equal rates, while sodium and lithium diffuse more quickly. The velocity of the positive ions of alkali salt vapours in flames appears to be about 60 cm. per sec. for 1 volt per cm.* at high temperatures.

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* H. A. Wilson, Phil. Trans. A. vol. cxcii. p. 499 (1899).

If these ions consist of atoms of the alkali metal, and if we suppose that the light emitted also comes from atoms of the metal, then we can calculate the charge carried by the atoms of the metal in the flame. We have the well-known equation

$$\frac{ne}{p}=\frac{k}{\mathrm{K}},$$

where e is the charge carried by one ion, n the number of molecules per c.c. in a gas at pressure p, k the ionic velocity, and K the coefficient of diffusion of the ions. If the metal atoms are only charged part of the time, then the observed value of the velocity will be kf, where f is the fraction of the time during which the atom is charged.

We have therefore $kf=60$. Hence for alkali salts in the flame

$$ne=\frac{60p}{\mathrm{K}f}.$$

In a previous paper I have given values of f deduced from the observed conductivities of flames containing salt vapours. The values found were

Cæsium	0·99
Rubidium..................	0·96
Potassium	0·91
Sodium	0·41
Lithium	0·21

Taking the temperature of the flame to be 2000° C., we get

$$n_0e=1{\cdot}8\times10^4\times\frac{2273}{273}\times\frac{p}{\mathrm{K}f}$$

in electrostatic units, where n_0 denotes the number of molecules per c.c. in a gas at pressure p and at 0° C.

Taking $p=1{\cdot}01\times10^6$ dynes per sq. cm., we get the following values of n_0e:—

	n_0e.	$n_0e\div1{\cdot}3\times10^{10}$.
Cæsium	$3{\cdot}47\times10^{10}$	2·67
Rubidium	3·58 ,,	2·75
Potassium	3·53 ,,	2·71
Sodium	3·21 ,,	2·47
Lithium	4·96 ,,	3·81

If we omit f in the expression for n_0e, we get the following for the average values over a long time of $n_0e \div 1{\cdot}3 \times 10^{10}$:

Cæsium	2·64
Rubidium..................	2·64
Potassium..................	2·47
Sodium	1·01
Lithium	0·80

$1{\cdot}3 \times 10^{10}$ is the value of the charge carried by the molecules in 1 c.c. of any gas at 0° C. and 760 mm. pressure, if each molecule carries the charge on one hydrogen ion in a solution.

It appears therefore that the average charge on lithium and sodium atoms in the flame is about equal to that on hydrogen ions in solutions, while the average charge on cæsium, rubidium, and potassium atoms is nearly three times greater.

It seems quite reasonable to suppose that alkali metal atoms which are very strongly electropositive should at the high temperature of the flame lose several electrons. In hot air at about 1400° C. it was shown by the writer that each atom of the alkali metals carries the same charge as that on one hydrogen ion, but the flame is certainly much hotter than 1400° C., and also the violent chemical actions in the flame might be expected to favour the escape of more electrons.

The well-known formula $k=e\lambda/mv$, where e is the charge on one ion, λ its mean free path, m its mass, and v its velocity of agitation, gives values of k for cæsium several times less than the observed value 60 when e is taken to be the same as that on one hydrogen ion in a solution. If we take e to be three times that on one hydrogen ion, then the formula $k=e\lambda/mv$ gives a value nearly equal to 60 for a cæsium ion. Very little weight, however, can be attached to this coincidence, because the formula $k=e\lambda/mv$ is probably only very roughly true, and also the value of λ is not known for alkali metal atoms in the flame. It has to be merely guessed at, and may easily be wrong by a factor of two or three. Also recent theoretical investigations indicate that the velocity of ions heavier than the surrounding gas molecules should be nearly independent of their mass. This agrees with the nearly equal ionic velocities and coefficients of diffusion found for cæsium, rubidium, and potassium.

As to sodium and lithium, the fact that their coefficients of diffusion are larger also agrees with the theory, for their masses are less than that of the molecules of the flame gases. That their ionic velocities are not also larger appears to be due to the fact that they are only ionized part of the time, so that the velocity observed is only an average, and is less than the velocity would be if they were charged all the time.

In conclusion, it may be said that the results obtained on the ionic velocities, coefficients of diffusion and conductivities of salt vapours in flames, seem to agree with the view that the positive ions consist of metal atoms having charges about three times the charge on one hydrogen ion in solutions. At the same time it must be pointed out that the possible error in the determinations of all these quantities is large; so that it is possible, but I think improbable, that the charge per ion is in reality equal to that on one hydrogen ion.

In a previous paper I gave reasons for believing that the positive ions due to salt vapours in flames are atoms of the metal. The arguments used in that paper are independent of the value of the charge carried by each ion so long as all the atoms when ionized carry the same charge. It has been suggested by Langevin that these ions are hydrogen atoms. This suggestion depends entirely on calculations of the ionic velocity by means of the formula $k=e\lambda/mv$. This formula cannot be relied on to give the velocity within a factor of at least two or three, partly owing to our ignorance of the true values of λ and partly because the formula itself is unreliable. No suggestion has been made as to how hydrogen ions are produced by salt vapours; and moreover the experiments made to determine the ionic velocities cannot be explained satisfactorily on the view that the ions are hydrogen atoms. Also salt vapours produce enormous conductivity in flames which contain no hydrogen. The increases of current observed in the determinations of the ionic velocities are nearly proportional to the conductivities due to the salt vapours, which shows that the ionic velocities measured are not those of a few special ions produced by some secondary reaction, but are the velocities of the majority of the ions due to the salts which must be formed from the salts, and therefore cannot be hydrogen.

IX. *On the Existence of Chemical Compounds of Short-lived Radioactive Elements.* *By* HANS SCHRADER, *Ph.D.*[*]

Introduction.

THE short-lived radioactive transformation products of radium, thorium, and actinium, which are included under the name of active deposits, do not differ fundamentally in their physical properties from the elements of

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[*] Communicated by Prof. E. Rutherford, F.R.S.

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long life such as uranium, thorium, or radium. Their electrochemical properties are similar to those of the common metals*. They appear to be present in solutions as ions, and it would, therefore, seem probable that they are capable of forming chemical compounds in the same way as the long-lived products. If these compounds do exist, evidence of their presence can be obtained from a study of some of their physical properties, a method usually employed in differentiating between homogeneous bodies. In the present case, where bodies present only in extremely small quantities are under examination, recourse has been had to an investigation of their volatility and their solubility.

Makower † has made some experiments on this point, and found that radium C, after being dissolved in hydrochloric acid and the solution evaporated to dryness, volatilized from surfaces of platinum and quartz in air at the same temperature as before such treatment. The result, therefore, indicates that, under the circumstances, radium C had not been changed chemically in such a manner as to be more or less volatile.

I. *Volatilization of Active Material from Surfaces of Different Substances.*

The amount of an active body which can be volatilized at a fixed temperature depends on the nature of the surface on which it has been concentrated. Thus Makower found that only 85 per cent. of radium C is volatilized from a quartz surface after heating it for 5 minutes to 1320°, while from a nickel surface 99 per cent., and from a platinum surface 96 per cent., is volatilized at 1200°.

Such behaviour is easily explained if one takes into account the fact that volatilization necessitates the separation of the molecules of the active material from the molecules of the plate on which they are deposited. So the process is influenced not only by the vibrations and molecular attraction of the volatilizing substance, but also by the corresponding forces of the molecules composing the surface from which the volatilization takes place. A further acceleration of the process may be produced by the gases and vapours, especially water, which rapidly condenses on every solid surface on which the active material may be deposited. The fact that the volatility varies if the surface in question is heated very strongly can be explained by these considerations. It is improbable that there exists an action between the different radioactive atoms themselves, for in the experiments described later the mean distance between two atoms of the material deposited on a platinum wire is about 10,000 times as large as their radii.

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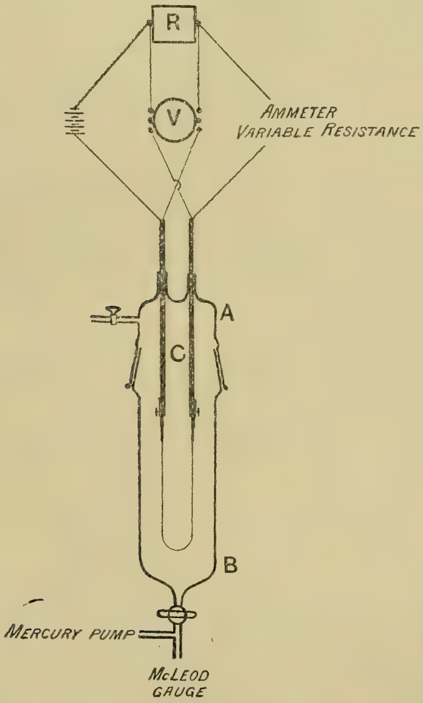
* v. Hevesy, Phil. Mag. xxiii. p. 628 (1912).

† Makower, Manchester Memoirs, liii. No. 7 (1909).

Volatilization of Actinium B.

According to the work of Levin *, actinium B is non-volatile below 400° but is completely volatilized at 750° in about 10 minutes from a surface of platinum. In the present paper this subject has been examined in greater detail. It has been found impossible to get perfect agreement in different experiments, but results have been obtained sufficiently definite to test whether any considerable change in volatility could be effected by chemical treatment of the active substance.

Experimental details.—A platinum wire 0·13 mm. thick, 10 cm. long, was bent into a loop the ends of which were welded to two thick platinum wires. The latter were soldered to copper rods fitting into two brass rods C, which were connected to the terminals of a battery. By means of screws perfect contact was ensured. The disposition is shown in the figure. The temperature of the wire was found by comparing the fall of potential along the wire with that



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* M. Levin, *Phys. Zeitschr.* vol. vii. p. 812 (1906).

along a constant resistance R (1·48 ohm) connected in series with the wire. The resistance of the wire was determined at 0°, 100°, and 443°. From these data the temperature of the wire was calculated according to Callendar's formula. The melting-point of some particles of pure sodium sulphate, which were heated on the wire in vacuo, was observed by means of a microscope, and found to be 895°. This was considered a sufficient test for the accuracy of measurements at high temperatures.

Before rendering the wire active, it was heated in vacuo for several minutes at 960°. It was then exposed to the emanation from an actinium preparation for 2 minutes. After 20 minutes, which is sufficient for actinium B, C, and D to obtain transient radioactive equilibrium, the activity of the wire was carefully determined in an α-ray electroscope. The amount of the activity was usually about 80 divisions per minute.

The wire was then inserted in the vessel AB, and heated at a constant temperature for several minutes at a very low pressure. The amount of active material volatilized was given by the difference in activities of the wire before and after heating, a correction being made for the decay of activity during the time which had elapsed between the two measurements.

Volatilization of Actinium B in vacuo.—The following are the results of experiments on the volatility of actinium B at different temperatures, at a pressure of ·003 mm. of air. The duration of heating was four minutes in all these experiments.

Temperature.	Per cent. of actinium B volatilized.
600°	Volatilization commences.
700°	10 to 20
800°	30 to 50
900°	90 to 98

Complete volatilization can only be effected at considerably higher temperatures. While the wire was being heated, the pressure in the vessel increased somewhat owing to the presence of the gas given off by the platinum. Special experiments showed, however, that this increase of pressure caused only a slight diminution in the amount volatilized at any temperature.

Pressures greater than 0·1 mm. were not used, since then the temperature of the wire could not be kept uniform owing to convection currents. The time during which the wire was heated naturally affected the amount of actinium B volatilized. If the wire were heated for 1 minute instead of 4 minutes at 900° only from 60 to 70 per cent. was removed.

Chemical Treatment of the Active Material.—In the following experiments, the active platinum wire was exposed for 10 to 15 minutes to gases and vapours which were thought capable of acting chemically on the active material. Hydrochloric, hydrobromic, hydriodic acids, bromine, and chlorine were used for this purpose. The gases were dried by sulphuric acid. Bromine, pure, from Kahlbaum, was used directly. The action of hydrochloric acid gas on the active material did not affect its volatility. Bromine, however, produced an increase in the amount volatilized at a given temperature. For instance, after treatment with bromine, the wire was heated for 4 minutes to 675° at a pressure of ·004 mm., 77 per cent. of actinium B was volatilized. From a wire not treated with bromine, on the other hand, only 18 per cent. volatilized under the same conditions of temperature and pressure.

It might appear possible that this increase in volatility is due to the action of the bromine on the platinum. Similar experiments in which quartz surfaces were used instead of platinum decided against this view. The experiments with quartz surfaces were conducted at atmospheric pressure in an ordinary electric furnace.

The following table shows some of the results:—

	Not treated.		Treated with bromine.	
Surface.	Temp.	Per cent. volatilized.	Temp.	Per cent. volatilized.
Quartz.	650°	24	660°	78
	655°	14	735°	82
	670°	55		
	890°	75		
Platinum.	660°	0	670°	69
	680°	2		

It is seen that bromine has the effect of increasing the volatility of radium B. The figures also show the influence of the surface on the volatility.

Chlorine and hydriodic acid also increased considerably the volatility both of actinium B and of actinium C. From a quartz surface after treatment with hydriodic acid, actinium C volatilizes at a lower temperature than actinium B. At 560°, heating for two minutes caused about 40 per cent. of actinium C to volatilize, but only 13 per cent. of actinium B. No more experiments were made, however, in this direction, since it could hardly be hoped that they would decide whether the change in volatility was due to a change in the active material itself, or in the surface only. It is possible that a very thin layer of water of thickness about 10^{-6} mm. which absorbs the gaseous acids may have a considerable influence.

In support of this assumption it may be added that, after treatment with gaseous hydrochloric acid, actinium B is more easily dissolved off a platinum surface by water than before such treatment. This is shown by the following experiments :—A strip of platinum was cleaned by placing it for a short time in boiling aqua regia. It was then heated in the blowpipe flame, and on cooling was boiled in a solution of ammonia. After it was heated again, it was exposed to actinium emanation for one minute. It was then kept in a slow current of gaseous hydrochloric acid for twenty minutes. Its activity was measured in an electroscope. The plate was then immersed in water for one minute and moved uniformly in it. It was dried with filter-paper, and the variation of its α-ray activity observed for the next twenty minutes.

Two experiments were carried out exactly similar to these two, except that the active material was not kept in an atmosphere of hydrochloric acid after exposure to the emanation, but kept in a desiccator for twenty minutes. One series of results obtained is as follows :—

Method of previous treatment.	Percentage loss of actinium B due to immersion in water during one minute.
1. Not treated with acid............	24
2. Do. do.	35
1. Treated with HCl which was dried with H_2SO_4	82
2. Treated with HCl which was dried with P_2O_5	81

The decay-curves obtained showed that the loss of activity was due almost entirely to solution of actinium B in the water. Only a very small quantity, if any, of actinium C was dissolved. The platinum surface had not suffered any visible change by this treatment. It appears, however, that a thin layer of acid is formed on the surface of the metal by the treatment, because the activity can be relatively easily removed from such a piece by rubbing. Incidentally it may be mentioned that actinium B is easily dissolved by acids even in very dilute solution. A concentration of ·001 normal hydrochloric or sulphuric acid is sufficient to dissolve in a minute more than 95 per cent. of the actinium B off a quartz surface, and more than 80 per cent. off a platinum one. Hardly any actinium C is, however, removed by this treatment.

It is obvious from the experiments described that the nature of the surface and of the surface-layer is an important but indefinite factor in the volatilization of minute quantities. For this reason experiments were made along a different line in which this factor is partly eliminated.

II. *Condensation Experiments.*

In the experiments which will now be described, the active material was first volatilized completely and the amount and composition of the material condensed on surfaces at definite temperatures investigated. It is to be expected that the active material would begin to condense as soon as it reaches a surface whose temperature is less than the volatilization-temperature. By this method volatility can be measured independent of any effect due to the surface-layer, since the condensation takes place at high temperatures.

The experimental arrangement was as follows:—The porcelain tube of an electric furnace placed vertically upright was closed at its lower end by asbestos and kieselguhr. Inside this was placed a quartz tube 32 cm. long and 1·1 cm. wide, closed at its lower end. The furnace was wound with a platinum wire in such a way that the temperature was highest at its lowest point and gradually decreased towards the other end. The active material was volatilized from a platinum surface, and was condensed on a thin long mica strip placed inside the quartz tube. The temperature of this strip at different points was determined by means of a thermocouple.

As soon as the furnace had reached a steady state of temperature, a small piece of very active platinum wire was dropped into the quartz tube. The temperature at the bottom of the tube was usually higher than 900°, so that the greater part of the material volatilized and was deposited again on the cooler parts of the tube and on the mica. After some minutes the latter was removed and cut into parts of equal lengths which were measured on both sides in an α-ray electroscope.

Experiments were conducted in air and in hydrogen. In experiments with the latter the tube was filled first with carbon dioxide and then with hydrogen. By means of a special device the active wire was dropped into the tube without opening it. The interval of time which was allowed to elapse between inserting the wire and removing the mica varied from 5 to 15 minutes in different experiments.

Volatility in Air.—The experiments showed the unexpected result that actinium B, after volatilization in air, becomes much less volatile than it had been when the experiments were conducted in vacuo. The details of one experiment are given in the following table :—

Interval of time between insertion of the active wire and removal of the mica, 5 minutes.

Length No.	Temperature.	Activity in div. per min.
0	Greater than 1090°	1200
1	1075° to 1090°	100
2	1045° to 1075°	2
3, &c.	less than 1045°	0

When a platinum strip was used instead of a mica one, an appreciable amount of activity was obtained above 1000°.

It thus follows that all the volatilized actinium B is deposited in air at temperatures above 1000°, although it begins to volatilize from a surface at 600°. Experiments with thorium B and C give the same results. A. S. Russell has carried out experiments for radium C and has shown that its behaviour is similar.

Volatility in Hydrogen.—The distribution of activity along the mica strip was found to be entirely different when the volatilization was carried out in an atmosphere of hydrogen. In contrast to the experiments with air the activity condensed on cooler parts of the mica, the maximum amount of actinium B being deposited between 615° and 675°. This is shown clearly in the following table :—

Interval of time between insertion of the active wire and removal of the mica, 15 minutes.

Length No.	Temperature.	Activity in div. per min.
0	Greater than 960°	8
1	945°–960°	8
2	925°–945°	9
3	880°–925°	5
4	820°–880°	3
5	760°–820°	4
6	675°–760°	84
Half of 7	615°–675°	780
Half of 7	555°–615°	5
8	385°–555°	10
9–11	200°–385°	5

Similar results were obtained with thorium B and C. Since the decay of thorium C is much slower than that of the corresponding member of the actinium series, it was possible to determine the ratio of the amounts of B and C deposited at different temperatures. Thorium B was deposited almost pure on the hotter parts of the strip, thorium C on the cooler. The latter product is consequently more volatile in hydrogen than the former. Further experiments on this point are in progress.

Conclusion.

It has been shown that the radioactive matter when once volatilized condenses on a surface at a much lower temperature in an atmosphere of hydrogen than in an atmosphere of air. This suggests that the active matter forms compounds in the presence of air which are less volatile and consequently easier to condense than the reduction products obtained in hydrogen, which are perhaps the elements, *i. e.* the metals themselves. The assumption is in agreement with the behaviour of common metals and their oxides, the former being generally more volatile than the latter.

The fact that the volatilization of actinium B from platinum, as shown above, takes place over a long range of temperature may be due to a partial oxidation of the active substance. Moreover, the very great volatility of the active deposit of radium in sealed quartz tubes observed by Russell *, as contrasted with the results of Makower †, is due to the fact that the former had hydrogen in his tubes. This point is treated by Mr. Russell in the following paper.

Summary.

1. The volatilization of actinium B deposited on platinum has been measured in a high vacuum and has been found to take place between 600° and 900°.
2. By allowing chlorine, bromine, hydrobromic acid, and hydriodic acid to act on the active material its volatility can be increased.
3. The B and C products of the active deposits of radium, thorium, and actinium condense in an atmosphere of hydrogen at a temperature several hundred degrees lower than in air. This has been explained by the formation of chemical compounds.

I wish to express my sincerest thanks to Prof. Rutherford for suggesting these experiments and for his ever ready advice and help.

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University, Manchester.

X. *The Volatility of Radium C* ‡. *By* ALEXANDER S. RUSSELL, *Carnegie Research Fellow of the University of Glasgow.*

THE interesting results described by Dr. Schrader in the foregoing paper show clearly that the constituent elements of the radioactive deposits are capable of forming chemical compounds. Dr. Schrader deals with the active deposits of thorium and actinium. In this paper, which is merely an appendix to his, the volatility of the radium active deposit is discussed.

Makower § has shown that radium A, radium B, and radium C cannot remain on a platinum surface when it is heated *in air* to temperatures of 900°, 600°, and 1200° respectively. From a quartz surface the least volatile product of

* Russell, Proc. Roy. Soc. A. vol. lxxxvi. p. 276 (1912).
† Makower, *loc. cit.*
‡ Communicated by Prof. E. Rutherford, F.R.S.
§ W. Makower, Manchester Memoirs, liii. No. 7 (1909).

the three, radium C, is not completely removed even by prolonged heating to 1320°. On the other hand, the author has shown * that in tubes containing impure radium emanation which has simply been pumped off from a radium solution, and sparked down, and which therefore contains an excess of *hydrogen*, radium A, radium B, and radium C are completely volatilized at a temperature of 650°. The apparent inconsistency between the two sets of observations is now very simply explained by Schrader's results. Makower determined the volatilization points of radium A, radium B, and radium C, under conditions such that part at least of each of the three products was oxidized. The author, on the other hand, determined the volatilization points of the bodies under conditions such that they were present, either as the elements themselves, or as compounds other than oxides. This is the chief reason for the differences in the two sets of results.

A few experiments confirming the truth of this conclusion will now be described.

Experiments in Oxygen.—A tube of clear quartz, 10 cm. long and diameter of section 0·5 cm., was filled with oxygen and about 30 millicuries of emanation. After the active deposit had been formed in equilibrium amount, the tube was placed in an electric furnace and heated, one end of the tube being at 650°, the other at 300°. After 15 minutes it was removed. Neither by electroscopic measurements of the γ-ray effect, nor by a fluorescent test with a screen of barium platinocyanide, could any change in the distribution of radium C be detected. The experiment was repeated with the hotter end of the tube at a temperature of 1200°. Again, after 15 minutes there was no appreciable change in the distribution of radium C. The volatilization point of radium C in an atmosphere of oxygen from a quartz surface is therefore greater than 1200°. This is consistent with Makower's results.

If the tube be heated at 900° or higher temperatures for an hour, a marked change in the distribution of radium C is effected. Now, if radium C were volatile at 1200° or at lower temperatures it is to be expected that some of it would be volatilized in 15 minutes. This result must therefore be explained by the growth of radium C from either radium B or radium A volatilized at 900°.

If the tube be heated at 700° for two hours, no change in the distribution of radium C is effected. Hence it follows that radium A, radium B, and radium C are all non-volatile in an atmosphere of oxygen below 700°.

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* A. S. Russell, Proc. Roy. Soc. A. lxxxvi. p. 244 (1912).

If the volatilization be conducted inside a similar sealed tube in an atmosphere of air, exactly similar results are obtained.

Experiments in Hydrogen.—Very different, however, is the character of the volatilization in an atmosphere of hydrogen. The original observation that all the products are volatilized at temperatures less than 650° was confirmed. Two more tubes were filled with impure emanation in the ordinary way and contain, therefore, in addition to hydrogen, carbon dioxide and aqueous vapour. In a third tube no aqueous vapour was present. A fourth contained only hydrogen and emanation. The results, however, on the volatilization of the active products were the same for all the tubes.

The volatilization point of radium C in hydrogen has been determined as follows:—The quartz tube was heated in such a way that the radium C was entirely removed to one end. This end was then inserted in the hottest part of an electric furnace which was varied in temperature between 400° and 700°. Under the circumstances the radium C is volatilized from the hotter end to a certain point at which it almost entirely condensed. In four experiments the mean temperature of the part of the tube at which it deposited was 360° ± 20°. If this part were then raised to a higher temperature, say 50° higher, the radium C would move further along the tube till it condensed on a part at a temperature of 360°.

This result is quite consistent with the results of the Royal Society paper, p. 245. There it is seen that radium C is completely removed from one end of a long tube to the other, provided the cooler end is at least at 400°. If it is at 320° it is not entirely removed. The temperature, therefore, at which radium C is condensed on a quartz surface lies between 400° and 320°.

This volatilization temperature was confirmed by another experiment.

The hottest part of a furnace was uniformly heated at 360°. A small tube containing emanation and hydrogen was placed inside the furnace so that one end was at a temperature of 360° and the other at 350°. The latter end was the nearer of the two to a β-ray electroscope. The β-ray activity (due, of course, to radium C) was measured for half-an-hour after insertion of the tube. The following is one set of results:—

Time in minutes	0	2	4	6	9	10	14	15	18	21	36
Activity in div. per min. .	33·6	33·6	34·3	35·3	36·0	36·8	36·2	43·5	43·5	43·7	45·0

It is seen that there is a sudden increase in the activity between the 14th and the 15th minute. This is due to the distillation of radium C to the cooler end of the tube as soon as the hotter end has reached 360°.

When the hottest part of the furnace was kept at 380° a similar experiment gave a similar set of results, the sudden increase occurring in this case after eight minutes. At 300° and at 200° no such effect was found. Radium C begins, therefore, to volatilize in considerable amount from a quartz surface in an atmosphere of hydrogen at about 360°. It is at this temperature also that it condenses entirely when volatilized at higher temperatures.

Experiments show that provided hydrogen is present with the emanation in excess of impurities such as carbon dioxide or traces of water, radium C volatilizes at the lower temperature; if oxygen is in excess, volatilization takes place at the higher temperature. Impurities such as dust or grease, which would undoubtedly hinder volatilization, can have no effect in these experiments, since the experiments are conducted in thoroughly cleaned, sealed quartz tubes.

The assumption of Schrader, that two different compounds of radium C are formed in the two sets of experiments, is the simplest explanation of a difference of more than 800° in the volatilization points of a body present only to the extent of about 7×10^{-10} of a gram.

Summary.

1. In presence of oxygen, radium A, radium B, and radium C are all non-volatile from a surface of quartz below 700°; the volatilization point of radium C is higher than 1200°.

2. In presence of hydrogen, radium A, radium B, and radium C are completely volatile from a quartz surface below 650°; the volatilization point of radium C is about 360°.

I have to thank Prof. Rutherford for his advice and help throughout this investigation.

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XI. *The Röntgen Radiation from Substances of Low Atomic Weight.*

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IT was found by early investigators that when a beam of X rays fell upon a substance an X radiation was excited in it. This secondary radiation, as it was called, varied with the nature of the substance in which it originated. With elements of low atomic weights, the excited radiation was approximately of the same type as the exciting beam. More recently[†], Barkla and Sadler have shown that from substances of atomic weight higher than 40, the secondary radiation is characteristic of the substance and consists in the main of one or more homogeneous beams. In the earlier experiments investigators were considerably handicapped by having to work with beams which were very heterogeneous and whose character was continually liable to variation. For example, when the secondary radiation from some particular element of low atomic weight was examined it was found to depend upon the kind of primary beam used. The discovery of the homogeneous beams offered an enormous simplification of the problem, since the character of these beams is quite definite and can be reproduced with certainty at any time. There is, however, one serious drawback in their use. The intensity of the homogeneous beams can only be a comparatively small fraction of the intensity of the primary beam exciting them. Under the most favourable circumstances the radiation scattered by a substance of low atomic weight is of feeble intensity, and when the exciting radiation is considerably weakened, as it is when we use homogeneous beams, special arrangements have to be made to measure the intensity and other properties of the scattered radiation.

The authors made use of the special form of electrometer described in previous papers, and found that by taking reasonable precautions they were able to obtain consistent results.

Carbon was chosen as a suitable substance to serve as a radiator.

In accordance with the results obtained by those who had used ordinary primary beams, we expected to find that the scattered radiation from carbon excited by a homogeneous beam would be itself homogeneous and of the same character as the primary, *i. e.* if we placed a thin sheet of absorbing material in the path of the scattered beam the percentage diminution in intensity would be equal to that occurring if the same sheet were used to cut down the primary beam.

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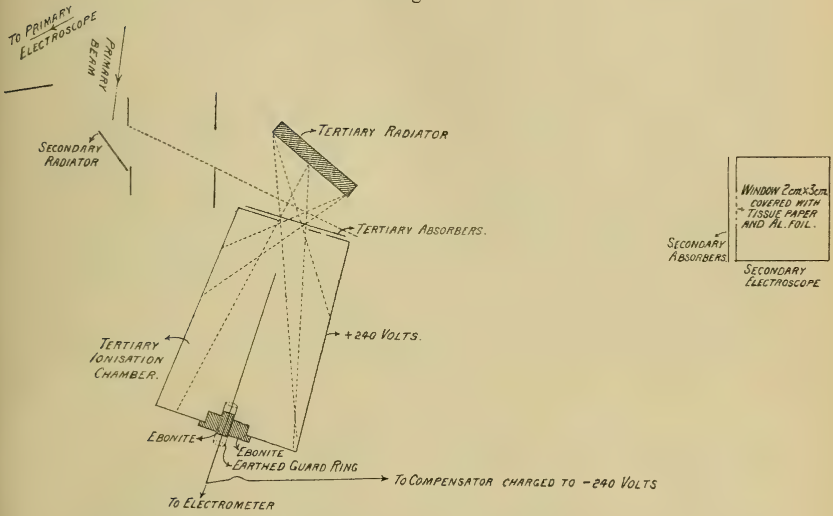
[*] Communicated by the Authors. Part of the expenses of this Research have been defrayed by a Government Grant.

[†] Barkla and Sadler, Phil. Mag. October 1908, pp. 550–584.

A reference to fig. 1, a diagrammatic representation of the apparatus used for making measurements, shows that the tertiary rays from the carbon enter the ionization chamber, on the whole, by more oblique paths than is the case with the secondary radiation, which consists of a nearly parallel beam. A correction must be made for this obliquity, since the length of path of the oblique rays in their passage through the absorbing substance is greater than that of rays which traverse the absorber perpendicularly, and thus a correspondingly greater relative absorption takes place. On the other hand, some of the oblique rays have only a small range within the ionization chamber, and thus do not contribute much to the ionization.

Fig. 1.



(An electroscope of the usual Wilson type received a small pencil of rays from the primary beam. In making measurements of the absorption of the tertiary beam, readings of the primary electroscope and the tertiary electrometer were taken before and after the introduction of the absorber into the path of the tertiary radiation. When testing the secondary radiation readings were taken on the primary and secondary electroscopes. By a suitable interpolation the corresponding readings on the secondary electroscope and the tertiary electrometer could be obtained at any time.)

Calculations based on careful drawings gave the order of correction to be expected, but its experimental determination was deemed more satisfactory. For this purpose a plate of pure copper was substituted for the carbon, and the absorption coefficient in aluminium of the oblique tertiary homogeneous radiation from it (excited by a more penetrating secondary beam) was found and compared with a nearly parallel homogeneous beam from copper when used as a secondary. The correction obtained in this case was in very close agreement with that obtained when other oblique homogeneous tertiaries of a more penetrating type were compared with the corresponding secondary parallel beams.

It was found when absorption experiments were carried out on the lines indicated above, that when all such corrections had been applied there was strong evidence that the radiation excited in carbon was heterogeneous, and distinctly *less penetrating* than the primary exciting beam.

The results are given in the following table:—

TABLE I.

Element giving sec. radiation.	Previous absorption of ter. radiation.	Percentage absorption of tertiary.	Percentage absorption of secondary.
Fe	nil	26·7	23·5
Cu	nil	32·4	
	50 p. cent.	29·2	25·3
	80 p. cent.	25·2	
Zn	nil	29·8	20·9
	50 p. cent.	25·7	
As	nil	21·8	11·9
	24 p. cent.	18·9	
	49 p. cent.	16·4	

Different thicknesses of aluminium were used as absorbers for the different beams, in order to keep down the absorption of the tertiary to approximately the same figure in each case.

The tertiary ionization was not sufficiently intense to enable the analysis to be pushed to extreme limits.

A glance at column 3, however, shows that the signs of heterogeneity are quite pronounced, while a comparison between columns 3 and 4 indicates sufficiently the degree of softening which has taken place.

The observed effects might be reasonably explained by any of the following hypotheses:—

(1) That there were impurities present in the carbon, presumably of a kind which would furnish secondary radiations of a softer type than that of the secondary exciting beam. The presence of such impurities would account for both the heterogeneity and the softer character of the scattered radiation as a whole. It was evident that the substances to be looked for were traces of metals of higher atomic weight than carbon or of their salts.

(2) That the exciting secondary radiation was imperfectly homogeneous and that a preferential scattering by the carbon of a soft constituent, which might be supposed to be present, took place.

(3) That carbon itself emits a homogeneous radiation which is feeble in character but very much softer than any of the exciting beams used.

These hypotheses were examined in detail.

Presence of Impurities.

A piece of the carbon used as radiator was carefully analysed, and was found to contain traces of iron but no perceptible traces of any other metallic substances. The amount of iron present was extremely small. To test how far this impurity and that of any other metallic compounds might explain the observed results, two similar carbon blocks were taken, one preserved intact and the other ground to a powder, and digested in a mixture of hot strong nitric and hydrochloric acids for several hours. The mixture was allowed to settle and the clear solution poured off. The residue was washed and further digested with strong nitric acid. Water was added, and the liquid was then filtered, and this residue carefully washed with distilled water and allowed to dry. The powder was made up into a radiator on a frame (this frame was carefully shielded from the secondary exciting beam) between two layers of tissue-paper. The two carbon radiators were now compared in their behaviour when subjected to the same secondary beam.

Identical results were obtained in each case within the limits of experimental error (a radiator made up of several sheets of tissue-paper behaved in a similar manner to a block of carbon).

Other substances besides carbon were examined, but not in such detail, *e. g.* a block of paraffin wax gave a softening effect, though not quite to the same extent as a similar block of carbon.

We were forced to conclude that this first hypothesis was no longer tenable. We had satisfied ourselves that in the powdered carbon no appreciable amount of metallic substance remained after treatment. The behaviour of paraffin and of paper appeared to negative the possibility of the softening in carbon being due to organic impurities. For had this been the case, we would have expected the softening to have been much more pronounced in paraffin than in carbon.

Heterogeneity of the Secondary Beams.

It has been shown in previous papers that the secondary radiation from substances like copper is nearly all of the characteristic type. It was pointed out that the radiation was remarkably homogeneous. This has been demonstrated in two ways. The first, the absorption method, showed that a thin sheet of aluminium, say, absorbed as nearly as possible the same percentage of a parallel secondary beam from copper, when the beam was reduced to only 5 per cent. of its original components by a suitable thickness of aluminium, as of the original beam. This method of analysis is not so sensitive as it might appear to be at first sight. For a nearly pure homogeneous beam with a slight admixture of other constituents differing slightly in hardness from the main beam would behave in much the same way when the absorption was pushed to this extent only.

The second method* depends upon the fact that the fluorescent radiation is only excited when the exciting radiation is of a more penetrating type than itself. Now a sheet of pure iron subjected to the radiation from a similar sheet of iron emits an extremely feeble radiation compared with that produced when it is subjected to a more penetrating radiation. But if the secondary radiation from iron had contained an appreciable amount of a soft constituent, this soft constituent would have been excited by the normal fluorescent radiation from iron. On the other hand, if the iron radiation possesses a constituent harder than the normal, it would excite the normal constituent from the second plate. The radiation so excited when iron radiation falls upon iron is as stated above very feeble in amount, and is on the whole slightly softer than the normal iron radiation. We must conclude, therefore, that if other homogeneous components coexist with the normal in the radiation from iron, they form relatively unimportant parts of the whole. If, therefore, the softened character of the radiation from carbon is to be explained in terms of the soft residual component of the beams from iron, copper, &c., we must assume that a substance like carbon is a much more efficient scatterer for soft radiation than for hard, especially as the softening effect becomes more pronounced when the hard exciting beams are used. In order to test this point, we used the secondary radiation from tin, which is known to consist of a very penetrating radiation, together with a component of appreciable intensity of a much softer type. If this latter is scattered to a greater extent by the carbon than the former, then since, if the secondary beam from tin is cut down by plates of aluminium before falling on the tertiary radiator, the soft radiation in the secondary beam disappears first, we should get a correspondingly rapid diminution in the intensity of the tertiary. The results of such an experiment are given in Table II.

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* Sadler, Phil. Mag. July 1909, pp. 107–132.

TABLE II.

Relative value of $\dfrac{\text{Intensity of tertiary radiation}}{\text{,, \quad ,, secondary \quad ,,}}$ for Tin radiation on Carbon.

Substance in path of sec. beam.	Deflexion of primary electroscope.	Deflexion of tertiary electroscope	Deflexion of secondary electroscope.	$\frac{\text{Prim.}}{\text{Sec.}}$	$\frac{\text{Ter.}}{\text{Prim.}}$	$\frac{\text{Ter.}}{\text{Sec.}}$
	43·0		10			
nil	46·0 44·8	10		4·34	·220	·956
	43·8		10			
	55·1		10			
·01 cm. Al	45·2 44·7	10		5·43	·222	1·20
	53·5		10			
	58·0		10			
·02 cm. Al	44·8 45·8	10		5·13	·221	1·29
	58·7		10			
	61·0		10			
·03 cm. Al	47·0 47·8	10		6·07	·211	1·28
	60·4		10			

It will be seen from columns 5 and 6 that while the secondary beam is cut down about 25 per cent. by a piece of aluminium ·02 cm. in thickness, the tertiary radiation is not perceptibly reduced, while three thicknesses of ·01 Al reduces the tertiary radiation by less than 5 per cent. But the soft radiation is practically all absorbed by the first two pieces of aluminium, for the first sheet absorbs 20 per cent., the second 7 per cent., while the third only 4 per cent. of the beam, which is about the amount by which a beam consisting solely of the hard constituent would be reduced by such a thickness of aluminium. But the ratio of the original ionizations produced by the soft and hard components respectively is at least as high as 1·5. If this relatively high proportion of soft radiation takes so small a share in the excitation of radiation from carbon, we are probably justified in concluding that the softened character of the carbon radiation cannot be explained by reference to any lack of homogeneity in the secondary beams used in these experiments.

Characteristic Radiation from Carbon.

That the effect was not due to corpuscular radiation from the carbon reaching the tertiary ionization chamber can be easily demonstrated, for the shortest distance between these two was at least 3 cm. But it was shown by one of us * that the most penetrating type of corpuscular radiation excited by a Röntgen beam failed to penetrate a distance of more than 2 cm. in air at atmospheric pressure. The experiment with tin as secondary suggested that hard rays were most effective in exciting radiation in carbon. It now became necessary to consider our third hypothesis—the possibility of there being a homogeneous radiation from carbon superposed upon the scattered.

It was evident that if we had a mixture of two homogeneous radiations—the scattered homogeneous secondary and the homogeneous tertiary characteristic of carbon—we could by suitable absorptions by sheets of aluminium find the absorption coefficient in Al of this latter component.

For let I_1 and I_2 be the relative intensities of the two homogeneous radiations. If α be the absorption by 1 cm. of air of the radiation I_1, and β that of I_2, the absorption in the electroscope of these two radiations will be proportional to

$$I_1(1-e^{-\alpha k}) \quad \text{and} \quad I_2(1-e^{-\beta k}),$$

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* Sadler, Phil. Mag. March 1910, pp. 338–356.

and the total ionization in the tertiary electroscope may be written

$$A[I_1(1-e^{-\alpha k})+I_2(1-e^{-\beta k})]$$

(A and k being constants of the electroscope; A including a correction for obliquity of the rays.)

$$= A[aI_1+bI_2] \text{ say.}$$

Let I_1' and I_2' be the intensities after the first absorption by a plate of aluminium. The total ionization in the electroscope will then be

$$A[aI_1'+bI_2'].$$

If λ_1 be the absorption coefficient of the unknown homogeneous radiation, and λ_2 that of the homogeneous secondary radiation, in aluminium, and x_1 the thickness of the first aluminium absorber,

$$I_1 = I_1' e^{\lambda_1 x_1} = m_1 I_1' \text{ say}$$

$$I_2 = I_2' e^{\lambda_2 x_1} = n_1 I_2' \quad ,,$$

If λ = the 1st *apparent* absorption coefficient of the mixed beam,

$$e^{\lambda x_1} = \frac{aI_1+bI_2}{aI_1'+bI_2'}.$$

Similarly, if i_1 and i_2 be the intensities, after a further absorption by a second plate of aluminium of thickness x_2, and λ' the second *apparent* absorption coefficient,

$$e^{\lambda' x_2} = \frac{aI_1'+bI_2'}{ai_1+bi_2}$$

and

$$I_1' = i_1 e^{\lambda_1 x_2} = m_2 i_1$$

$$I_2' = i_2 e^{\lambda_2 x_2} = n_2 i_2.$$

Substituting, we have

$$e^{\lambda x_1} = \frac{am_1 I_1' + bn_1 I_2'}{aI_1'+bI_2'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$e^{\lambda' x_2} = \frac{aI_1'+bI_2'}{\frac{aI_1'}{m_2}+\frac{bI_2'}{n_2}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

from (1)

$$\frac{I_1'}{I_2'} = \frac{b}{a} \cdot \frac{(n_1 - e^{\lambda x_1})}{(e^{\lambda x_1} - m_1)}$$

and from (2)

$$\frac{I_1'}{I_2'} = \frac{b}{a} \cdot \frac{\left(1 - \frac{e^{\lambda' x_2}}{n_2}\right)}{\left(\frac{e^{\lambda' x_2}}{m_2} - 1\right)},$$

and hence

$$e^{\lambda' x_2}[m_1 m_2 - n_1 n_2] - e^{\lambda x_1 + \lambda' x_2}[m_2 - n_2] - m_1 m_2 n_1 + m_2 n_2 n_1 = 0. \quad (3)$$

If $x_1 = x_2 = x$, *i. e.*, if the same thickness of absorbing material be used in obtaining the same successive absorptions,

$$m_1 = m_2 = m$$

and $$n_1 = n_2 = n$$

and equation (3) reduces to the simpler form,

$$m^2[e^{\lambda' x} - n] + m[n^2 - e^{x(\lambda + \lambda')}] - n^2 e^{\lambda' x} + n e^{(\lambda + \lambda')x} = 0.$$

All the quantities in this equation are known, and since

$$m = e^{\lambda_1 x},$$

λ_1 the unknown absorption coefficient of the second radiation may be calculated.

To test the order of accuracy to be obtained by using this formula, a mixed radiator of Cu and Fe was made up and subjected to the radiation from As, the mixed tertiary beam in this case consisting essentially of the homogeneous radiations characteristic of Fe and Cu. A sheet of paper, placed in the path of the tertiary beam, gave a first absorption of 37·0 per cent. A similar sheet of paper was then placed in the path of the beam, and a second absorption found with the first sheet of 35·5 per cent. (this method ensures that x is the same for each absorption). Taking the absorption coefficient of the Cu radiation as known to be 129, and supposing that of the Fe radiation to be unknown, we have

$$e^{\lambda x} = 1{\cdot}5873 \; ; \; e^{\lambda' x} = 1{\cdot}5504 \; ; \; n = 1{\cdot}3890,$$

substituting these values in the above equation,

$$m = 1{\cdot}904.$$

From this, we get as a value of the absorption coefficient for the Fe radiation,

$$= \frac{129 \times \log(1{\cdot}904)}{\log(1{\cdot}3890)}$$
$$= 253$$

against a known value for Fe radiation of 239.

Other test cases were taken, and the formula found to be reliable to within about 10 per cent.

To ensure accuracy it was necessary to secure that no one constituent had been completely absorbed by the two absorbing layers. It was important also that the difference between the two apparent coefficients should be as great as possible. Having regard to these two points a piece of carbon was taken and subjected to homogeneous beams of varying hardness. Assuming that the tertiary radiation in each case consisted of secondary radiation scattered as a homogeneous beam of unaltered hardness, together with a radiation characteristic of carbon, the absorption coefficient of the latter in aluminium was calculated from the observed absorptions.

The results of these experiments are given in the following table:—

TABLE III.

Source of Secondary radiation.	λ for Secondary radiation.	Calculated value of λ for the soft Tertiary radiation.
Cu	128·9	319
As	60·7	315
Sr	24·6	184
Mo	12·7	165
Ag	6·75	125
Sn	4·33	70

Note.—The values of λ in column 2 are for radiations filtered through appropriate thicknesses of aluminium.

In the case of those secondary beams known to contain a soft constituent, this was removed by first passing the radiation through absorbing sheets of aluminium before it fell upon the tertiary radiator.

A glance at column 3 shows at once that after making due allowance for experimental error there is no semblance of agreement between the values of λ.

We must then abandon our hypothesis as to the composition of the tertiary beam. There is no precedent for supposing that if a characteristic radiation were emitted by carbon it would be other than homogeneous. Moreover, experience justifies us in concluding that in such a case its degree of hardness would be constant and independent of the hardness of the exciting radiation.

It is well known that some substances have more than one type of homogeneous radiation. It is possible that carbon is one of these, though the balance of evidence on the whole makes it improbable that an explanation of the phenomena lies here. The authors incline more to the belief that an actual modification of the X ray occurs in its passage through matter, a general softening taking place. Other evidence favouring this view is accumulating along rather different lines in a separate investigation, the details of which are not yet ripe for publication. One thing appears to be firmly established, viz., the harder the rays, the more profoundly are they modified in their passage through matter.

An extension of an experiment described in an earlier paragraph seems to bear upon this point. It was pointed out that the radiation from tin consisted of two parts, a soft component having a value for λ in aluminium about 40–50 and a hard component for which λ is about 4·0. It was also shown that the *intensity* of the tertiary radiation excited in carbon depended chiefly upon the hard component. On testing the *quality* of the tertiary radiation, it was found that this too was practically unchanged when the soft component was suppressed. It was found impossible to determine to what extent the tertiary excited by the hard component from tin was heterogeneous, owing to the feebleness of the ionization it produces. The disturbing effects of stray radiations become more pronounced when dealing with a residual ionization.

No claim for accuracy is put forward with regard to the values of λ given in column 3, Table III. For if the radiation prove to be non-homogeneous it is obvious that they can only represent average values. There can be no doubt, however, that a homogeneous beam is not scattered solely as a homogeneous beam, even if at all. The experiments described do not enable us to determine whether there is a homogeneous radiation emitted by carbon. It is highly probable that such a radiation does exist, though of feeble intensity.

It is hardly necessary to point out that a clear solution of this problem is bound to have an important bearing on the theory of the production of an X ray. Incidentally, the bearing of these results upon such questions as the polarization and the general distribution of a scattered radiation will need to be carefully considered.

It is perhaps only fair to mention that, as far as we can judge, the primary heterogeneous beams used in the earlier experiments on scattering were generally of a soft type.

When we consider that the constituents of any one such beam would have a wide range of hardness and that the hardest constituents are more effective in transforming the incident radiation, it is not to be wondered that on the whole the scattered radiation behaved as a primary weakened in intensity only.

The authors recognize that their experimental data are somewhat fragmentary and fail to provide a complete solution of this peculiarly elusive problem. It was thought, however, that the results already obtained contained sufficient novelty to warrant publication.

Summary.

It is shown that: (1) A homogeneous beam when scattered by a substance of low atomic weight is transformed into a softer type of radiation.

(2) The harder the exciting beam, the greater is the intensity of the scattered radiation.

(3) The harder the exciting beam, the more profound is the change in its quality.

In conclusion we wish to thank Professor Wilberforce for placing the resources of the laboratories at our disposal.

The George Holt Physical Laboratories.
January 1912.

XII. *Studies in the Photometry of Lights of Different Colours.*

By Herbert E. Ives[*].

[Plates III.-V.]

I.

Spectral Luminosity Curves obtained by the Equality of Brightness Photometer and the Flicker Photometer under similar conditions.

Synopsis.

Introduction.
  1. *Difficulties in determination of luminosity in the presence of colour difference.*
  2. *Existing methods of heterochromatic photometry.*
    - *a.* Equality of brightness.
    - *b.* Visual acuity.
    - *c.* Critical frequency.
    - *d.* Flicker photometer.

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[*] Communicated by the Author.

3. *Requirements of a good method of measurement.*
    - *a.* Sensibility.
    - *b.* Summation quality.
    - *c.* Useful value of quantity measured.
4. *Degree to which these requirements are met by existing methods.*

    Equality of brightness and flicker methods meet requirements much better than other methods, with apparent advantage in flicker method of greater sensibility. Different results obtained by these two methods indicate importance of a comparison between them.
5. *Physiological factors to be considered.*
    - *a.* "Purkinje" and "yellow spot" effects. Rods and cones.
    - *b.* Colour blindness.
    - *c.* Adaptation and fatigue.

SPECTRAL LUMINOSITY CURVES AS OBTAINED BY FLICKER AND EQUALITY OF BRIGHTNESS PHOTOMETERS.

1. *Previous Comparisons.* Dow, Stuhr, Millar, Wilde.

    Apparent differences in the magnitude of Purkinje and yellow spot effects with the two photometers.
2. *Apparatus and Procedure.*

    Arrangements for securing monochromatic spectral colours at various illuminations and with various sizes of the field of view. Details of measurements.
3. *Measurement.*
    - *a.* Sensibility.
      Greater sensibility by the flicker method. Flicker speeds.
    - *b.* Reproducibility of measurements.
      Greater reproducibility by the flicker method.
    - *c.* Effect of changing illumination.
      "Purkinje effect" by equality of brightness, reverse effect by flicker.
    - *d.* Effect of changing field size.
      "Yellow spot" effect at low illumination by equality of brightness, reverse of this effect by flicker.
    - *e.* Relative positions of flicker and equality of brightness curves.
      Nearest each other at high illuminations and with small fields.
      Areas of two kinds of luminosity curves different.
    - *f.* Comparative results obtained by different observers.
4. *Theoretical Considerations.*

    Significance of Purkinje and opposite effects. Bearing on theory of rod and cone action. Insufficiency of present theories. Future work indicated.
5. *Bearing upon Practical Photometry.*

INTRODUCTION.

ANY light may be defined in terms of hue, saturation, and luminosity. Practical photometry is concerned primarily with luminosity. But that quality of light cannot by simple means be separated from the other two. The eye can equate but cannot appraise. Hence the eye is on uncertain ground whenever it attempts to compare the luminosities of lights of different hue or saturation. This difficulty has long been recognized, and various opinions as to the solvability of the problem have been expressed. Various plans to accomplish its solution have been proposed. The belief has been expressed by some that comparison of the luminosities of two differently coloured lights is no more possible of exact accomplishment than the exact comparison of a sound with an odour. Helmholtz declared his lack of confidence in his own ability to make such comparisons. On the other hand, some observers have by practice acquired skill and apparent certainty in heterochromatic photometry. Again, methods of photometry have been discovered and developed which, in the process of measurement, evade and perhaps eliminate the differences in hue and saturation.

By these different methods different criteria for equality of luminosity are obtained. What are the relations between the criteria? Are two coloured lights which are equally bright as measured by one method, of equal brightness as measured by another?

The relative brightness of differently coloured lights is not constant under all conditions. Physiological factors enter to a large degree. The "Purkinje effect" is the name given to the increase of blue sensitiveness at low illumination. The "yellow spot effect" is the name given to the change in the relative brightnesses of different colours occurring when the size of the field of view is changed. To what degree do these enter in the various methods of colour photometry?

The advent of high efficiency incandescent lamps and of new illuminants with wide range of colour, the prospect of an even greater variety of illuminants in the future, diverging still further in colour from the present flame and carbon lamp standards, all render the problem of measuring the luminosity of lights of various hues one of the most important in photometry. A complete solution of the problem can come only through knowledge of the relative behaviour of each method of comparison under the various conditions known to affect the relative brightness of different colours. That knowledge acquired, we may proceed to a process of test and selection, and so hope to determine that method which meets to the fullest degree the requirements of a method of measurement.

The chief obstacle in the way of giving preference to one method of colour photometry over another is at present our lack of data. Some forms of flicker photometers have been compared with some forms of direct comparison photometers. Spectral luminosity curves for the eye have been derived by tests of visual acuity, by the flicker photometer, by equality of brightness methods, and by the determination of critical frequency of flicker. But such investigations have been carried out by different observers, using different conditions of illumination and different colour standards, with instruments whose dimensions were different in essential particulars. And frequently some of the most important conditions have not been stated. Prominent among these should be mentioned the illumination and the size of the photometric field.

It is the object of the present studies to obtain data for the solution of this problem. For this purpose comparisons will be made between the various methods. The different factors which influence the relative luminosity of colour will be systematically varied as each method is studied. The same conditions will, however, be maintained throughout, whereby satisfactory comparisons of the different methods will be possible. Attention will be devoted chiefly to the most promising lines of investigation, and ground covered by previous workers will not be touched unless coordination of their work with the present work is found impossible. Problems incidental to the main questions will be investigated where necessary, but the ultimate object to be held in view will be the determination of the most satisfactory method of measuring luminosity where differences of colour exist.

Existing Methods of Heterochromatic Photometry.

The chief methods of light measurement which have been applied to differently coloured lights are :—

1. *The method of equality of brightness.*—The two lights illuminate the two parts of a photometric field. The relative intensities of illumination from the two lights are changed until the two differently coloured fields give a sensation of equal brightness. The illuminations are then called equal.

2. *The method of visual acuity.*—Two illuminations are equal when the same fineness of detail is just distinguishable by each.

3. *By critical frequency.*—Two illuminations are equal when the flicker produced by rapid alternation of one illumination with black disappears at the same speed of alternation as for the other when similarly alternated.

4. *The flicker photometer.*—Two illuminations are equal when upon rapidly alternating one with the other no sensation of flicker results, the speed of alternation being such that the slightest change of either illumination produces a flicker.

The Requirements of a Good Method of Measurement.

As a preliminary to an investigation of these methods of measurement, the requirements necessary to a satisfactory method should be kept clearly in mind. These are, first, that the range of possible settings of the measuring instrument shall be small; that is, the method shall be as definite as possible. In the photometry of lights of the same colour, for instance. the range with a Lummer-Brodhun contrast photometer is of the order of one per cent. Second, that the quantities to which values are given by the measurements shall behave as arithmetical or physical quantities. This involves that quantities measured as equal to the same thing shall measure equal to each other, and that the sum of the parts shall be equal to the whole. This second requirement of a method of measurement is not one often dwelt upon in the measurement of purely physical quantities, because such quantities naturally fulfil the requirement. In dealing with physiological quantities, however, it cannot be assumed without proof that this is true. As a third requirement in the present case may be added that the values given to different colours shall represent as nearly as possible their useful value as light. In explanation of this last requirement it will suffice to point out that the first two requirements, which pertain to any method of measurement, would be met by simple measurement of the energy radiated. Light, however, considered as a sensation, is represented by very different quantities of energy at different wave-lengths in the visible and invisible spectrum, and such a measurement would not give a number to the light value. Or, again, if there exists a fundamental quantity of brightness, which can only be separated and measured under very special conditions, this measurement, while perhaps satisfactory to the psychologist or physiologist, would not satisfy the photometrist, who is interested in light as used for illumination, even if the underlying real brightness quality is masked by other qualities such as hue. What is therefore required is a method of measuring lights of different colours with the same order of definiteness which pertains to strictly physical measurements, using units which may be dealt with as physical quantities, but yet yielding values closely representing the values of the lights for illumination, for good seeing, or as producers of the sensation of brightness.

Degree to which these Requirements are met by Existing Methods.

Comparison of the brightness of two fields of different colour is a somewhat uncertain and unsatisfactory process.

The difficulty is largely psychological. A decision must be formed as to when a certain quality of the two illuminations is equal, while other inseparable qualities are different. With a large colour difference, this decision is difficult; at first attempt almost impossible. At best, one's settings are apt to vary over a wide range; at another time a different decision may be made, and the average of a set of readings diverge considerably from the set previously made. With small colour differences an observer will with practice make quite definite settings, and his criterion of equality then probably assumes a fairly constant value. As a method of heterochromatic photometry, the method of direct comparison is principally open to objection because of its lack of definiteness of setting.

As to the second requirement, that the measured light quantities may be treated as physical quantities, *i. e.*, compared in any order or added to produce their arithmetical sum, Abney with his colour-patch apparatus has measured the intensities of several spectral colours separately and then together, finding practically perfect agreement between the sum of the intensities and the intensity of the sum. In view of the difficulty of making exact settings with coloured fields, those results show remarkable agreement. It is to be regretted, however, that these measurements were made with such an inexact instrument as a shadow photometer, that the illumination from the different colours (an arc spectrum) was very different, and that the measurements were confined to very small fields: in short, that they were made under conditions quite different from ordinary photometry.

As to the method of visual acuity, its chief defect is extreme lack of definiteness. Properly it should be used only for determining different orders of illumination. Visual acuity varies as the logarithm of the illumination and very slowly. For instance, with the best test objects probably a 5 per cent difference in visual acuity represents the limit of perceptible difference. Study of Kœnig's data on the relation between visual acuity and illumination shows that this corresponds in the middle region of illumination studied to about 30 per cent. difference in illumination. As a method of measuring illumination, visual acuity is therefore almost beneath notice. This is borne out by the work of all observers; so that while visual acuity may be a correct measure of good seeing conditions, it is not a method of photometry. Until, therefore, it shall be proved that the criterion of good seeing as so determined is very different from that given by other methods, and much more important, visual acuity would not appear to deserve much attention. To the writer's knowledge no measurements are on record which were made to determine whether the arithmetic sum of two differently coloured illuminations measures equal to the two illuminations together. One advantage the method of visual acuity has over that of equality of brightness, is that by the nature of the criterion two illuminations equal to the same are assuredly equal to each other. This fact depends of course on the illuminations not being compared one with another, but with, as it were, an outside standard of different character. The importance of this will depend on whether in other methods any error is shown due to characteristics of the compared lights, other than their luminosity.

Measurement of illumination is possible by determining the critical frequency of flicker. The method is subject to very much the same criticisms as apply to measurement by visual acuity. Taking as illustration the investigation of Kennelly and Whiting, we find that "every time the illumination on the target is doubled, the mean vanishing flicker frequency increases by 3·3 cycles per second approximately." The observations of each observer used to obtain the mean of three show sometimes values 1½ or 2 cycles per second above the mean adopted, sometimes as much below, indicating a possible range in settings corresponding to about 100 per cent. in illumination. In short, the method appears to be not so much for accurate light measurement as for orders of illumination. It possesses the characteristic noted in connexion with visual acuity methods, namely, that it is not necessary to view the two differently coloured fields simultaneously in order to make a measurement; two illuminations equal to a third are, therefore, of necessity equal to each other. Tests of the results of adding illuminations of different colours are lacking.

A word may be said in passing in regard to the common characteristic of the last two methods, that by neither is it necessary to juxtapose the observed illuminated surfaces. In one way this is an advantage. The problem of judging between two hues is eliminated. Judgment is made on a quality common to both illuminations (their detail or flicker revealing power) which is not confused by hue, as is the sensation of brightness. On the other hand, both visual acuity and ability to perceive flicker are largely influenced by physiological conditions such as adaptation and fatigue, and are apt to vary from time to time. The uncertainties introduced by these latter are probably as great as the uncertainties of individual settings during one measurement. At any rate it is significant that none who have worked with either visual acuity or critical frequency in their relation to illumination have seriously proposed using them as means of exact photometry.

The last method to be considered is that of flicker photometry. The flicker photometer owes its applicability to heterochromatic photometry to the fact that colour fusion occurs before brightness fusion; that is, the sensation of flicker caused by alternation of one colour with another disappears at slow speeds of alternation, resulting in a field of uniform hue in which is an outstanding flicker. This outstanding flicker disappears only when the two illuminations bear a certain relation to each other. For lights of identical colour the point of disappearance of flicker corresponds exactly with the point of equal illumination. With lights of different colour this point certainly corresponds closely with equality as measured by other methods, though perhaps not exactly.

The flicker method has found many advocates because of its superior definiteness as compared with the method of direct comparison. The comparison of different hues is eliminated, apparently by a process which separates luminosity from hue, leaving a phenomenon—flicker—of considerable delicacy. Whitman, Rice, and others find settings between lights of different colours nearly as easy as between lights of the same colour. The accuracy of setting compares well with that of direct comparison between lights of the same colour.

Work by Whitman and Tufts would appear to show that the flicker method possesses this further requirement of a method of measurement: that several illuminations acting together measure to the arithmetic sum of their values measured alone. In short, the flicker method appears to yield greater definiteness than the method of equality of brightness, and to have the same qualifications of a method of measurement as Abney's work would show for the latter. Spectral luminosity curves obtained by the flicker photometer have shown considerable similarity to those by other methods, so that the special requirements of a method of coloured light photometry appear to be well met.

From this review it seems that the study of methods of heterochromatic photometry would most profitably centre around the equality of brightness and flicker methods. Concensus of practical opinion agrees with this, for it is with the different values given by these two methods that photometrists are now largely concerned. From the manner in which each meets the requirements outlined above, it might seem as if both are suitable, with the advantage in favour of the flicker method because of its greater definiteness. It might be expected too that the methods would agree. Yet apparently this last is not the case. The flicker method has not been so generally used as its convenience would recommend, because numerous disagreements have been recorded between its renderings and those of the longer established method of direct comparison or equality of brightness. The explanation of these differences is most likely found in the different conditions which have obtained when the characteristics of the two methods have been studied, and when comparisons have been made between them. The importance of certain physiological conditions will be emphasized in the next section. The most significant facts are that the methods do not in general agree, and that the tests to which they have been subjected, in particular by Abney and by Tufts, were under conditions radically different than those of practical photometry. The most pressing subject for investigation just now is, therefore, the relation between these two methods, under various conditions. What the important conditions are will be made clear by consideration of certain physiological factors.

Physiological Factors.

The relative sensibility of the eye to different coloured lights is considerably affected by changes in illumination and by changes in the size of the field of view. According to present theory, these differences are due to the irregular structure of the retina and to the preponderance of different seeing elements at different illuminations. Two sets of elements are present in the retina—rods and cones. According to the " Duplicitäts Theorie " of von Kries, the rods are chiefly responsible for vision at low intensities, the cones at high. The cones are sensitive to colour with a maximum of sensibility in the yellow ; the rods are not sensitive to colour, but have a maximum of sensibility at a wave-length corresponding to the green. These elements are distributed unevenly over the retina. At the centre (the fovea) there are no rods; both rods and cones are about equally distributed in the surrounding central region called the *macula lutea*; while in the outer regions of the retina rods predominate. Hence, either increasing the size of field or decreasing the illumination brings into play more of the rods, thereby explaining the Purkinje and yellow-spot effects.

Whether the rod and cone theory will prove the true explanation of retinal action is not at present of great moment. The facts about retinal structure on which it is based are, however, to be kept in mind while studying colour photometry, as indicating the most probable critical points in the series of changes which may be rung on conditions.

The complications introduced by colour blindness will not be a main topic of the present research. The object will be to secure data from normal eyes, on the understanding that only observers of normal vision are equipped for photometry with lights of different colours. The comparison of various methods with one another, and the investigation of each as to its qualifications as a method of measurement, can be made by one observer, and in fact should be so made first of all, as thereby differences in method are not confused with differences between observers. Some data obtained by several observers of normal vision have however been collected with a view to testing the generality of the phenomena found, and to determine how much variation exists among observers with no marked abnormalities of vision.

Adaptation and fatigue are probably the physiological factors most difficult to estimate and control. Colour vision is peculiarly dependent on adaptation. When physiologists work on problems of vision they distinguish between the light-adapted eye and the dark-adapted eye, depending on whether the eye works in the light or in comparative darkness. The ability to perceive colour, which is lost on greatly decreasing the illumination, gradually returns as the eye becomes accustomed to the small quantity of light. Fatiguing the eye for one colour makes it more sensitive to others. Fatigue also alters the relative critical frequencies of flicker for different colours; and the effect is different depending on the character of the fatiguing light.

Both these disturbing factors must be kept in mind when investigating heterochromatic photometry, but their detailed investigation must wait until the more prominent phenomena have been covered. It is to be noted that the effects of adaptation and fatigue are brought out by extreme conditions, such as very high or very low illumination. In ordinary photometry the eye is probably in the condition called by physiologists "light adapted," because of the order of illumination used, and because of the use of auxiliary lights for such things as scales and data sheets. If observation has not been too long continued or if the illumination is not trying, the effects of fatigue may be kept at a minimum. The policy in the present investigation has been to maintain the conditions of lighting at nearly those of practical photometry, and, by making observations for only a limited time each day, to prevent the eye from becoming fatigued to such an extent as to be noticed by difficulty or discomfort in making readings.

Summarizing the physiological considerations we find that an investigation of heterochromatic photometry must include studies of the effect of varying the size of the photometric field and of varying the illumination. A complete study will include observations for a large range of illuminations and for several sizes of field at each illumination. The state of adaptation of the eye must be as nearly as possible that holding under the conditions of measurement to which results are to be applied.

I.

SPECTRAL LUMINOSITY CURVES AS OBTAINED BY FLICKER AND EQUALITY OF BRIGHTNESS PHOTOMETERS.

Previous comparisons of the two photometers.—The most extensive comparisons heretofore made between these photometers are those of Dow and Stuhr. Comparisons of less complete character have been made by Millar, Wilde, and others. Dow, recognizing the importance of the physiological factors above emphasized, has studied the effects of change of illumination and of field-size. For this purpose he used coloured glasses over his light sources. Comparing, for instance, red and green lights, he found by direct comparison that on decreasing the illumination the relative brightness of the red decreased, the decrease being very rapid from ·2 metre candle down. With the flicker method this decrease was hardly observable, and the change at ·2 metre candle was not shown, although the difficulty of flicker measurements is too great at low illuminations to establish this difference with certainty. On decreasing the size of the field, at a fixed illumination, the brightness of the red increased by equality of brightness ; by the flicker method a much smaller increase was found. These experiments were carried out with the same sized field and the same illumination for each method, so that on that score the results are beyond criticism. They indicate that the flicker method is less susceptible to the influence of changed illumination or size of field.

Stuhr has compared the methods of visual acuity, direct comparison, critical frequency, and flicker, using coloured glasses. He found the methods by critical frequency and by flicker to yield identical results. These differed both from the results of visual acuity and equality of brightness measurements, lying between these latter. Different field-sizes —unspecified—were used for visual acuity and other measurements, and in no case was attention paid to the absolute illumination. In other words, the physiological factors were not considered.

P. S. Millar describes measurements of a mercury arc against incandescent lamps in which the illumination varied over a wide range. With equality of brightness photometers the mercury arc measured relatively much brighter at low illuminations: with flicker photometers this effect was absent.

Wilde describes measurements of a tungsten lamp against a carbon, made with a flicker photometer and with an equality of brightness photometer. The photometers showed a disagreement of several per cent.

Of these comparisons that of Dow is by far the most complete and scientific, establishing as it does that the two methods give different results for the same size field when the illumination is changed, and that at a fixed illumination they respond differently to changes of field-size. The two points in which Dow's work is incomplete hold also for the work of the other investigators quoted, while their work is less complete in other ways. First, it is to be noted that the experiments refer to no definite scale of colour, such, for instance, as the spectrum. It is therefore impossible to calculate from his results the magnitude of the effects of varying conditions for any given energy distribution. Second, while the effect of varying either illumination or field-size was investigated, the investigation was not continued to the point of varying both together. There is, for instance, a large range of illuminations suitable for the carrying out of measurements. At each of these illuminations any one of several sizes of field may be used. Our knowledge of the relative behaviour of the two methods is incomplete until we know, on some definite colour scale, how these two variables—illumination and field-size—affect the criteria furnished by the methods, for all practicable combinations of the variables. The importance of this knowledge may be indicated by considering the character of the differences between the methods as indicated by Dow's work:—

The Purkinje effect is less with the flicker method. We also know from the work of Kœnig and Brodhun that the Purkinje phenomenon practically disappears for high illuminations. The effect of decreasing field-size is (according to Dow) less for the flicker method, but we also know that the Purkinje effect by direct comparison has been found much less for small fields. That is, by using high illuminations and small fields the differences between the methods are less than for low illuminations and large fields. At once there opens the possibility that by proper choice of illumination and field-size the two methods may agree. Should this be the case, it would be a strong argument for choosing that illumination and field-size as the standard one for making colour comparisons. The possibility thus indicated is sufficient for undertaking a complete comparison of the methods.

Apparatus and Procedure.

The method of attacking the problem was to determine by the two methods and under various conditions the luminosity curves of a spectrum of known energy distribution. The apparatus used is similar in some respects to that of Tufts, and is shown in fig. 1. A Hilger constant-deviation

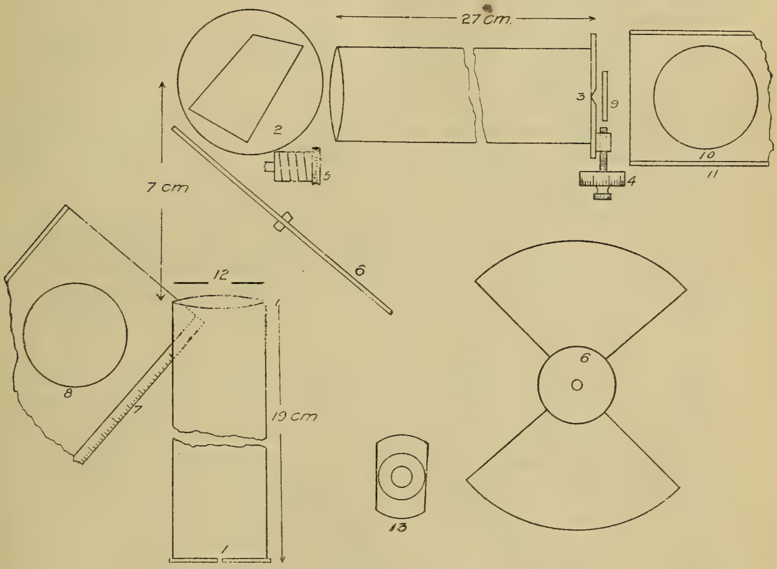

Fig. 1.—Arrangement of Apparatus.

1. Observing slit.
2. Prism table.
3. Collimator slit.
4. Divided drum.
5. Wave-length drum.
6. White sector-disk.
7. Photometer bench.
8. Standard lamp.
9. Diffusing glass.
10. Light source.
11. Photometer bench.
12. Diaphragm.
13. Diaphragms used.

wave-length spectrometer forms a spectrum of the light source upon an eye-slit (1) of dimensions $\frac{1}{2}$ by 2 mm. The eye placed at this slit observes the prism face (2) illuminated by monochromatic light of a purity determined by the relative size of collimator and eye-slit (3 and 1). The wave-length incident on the eye-slit is changed by motion of the drum (5). The size of the collimator slit is changed by turning the drum (4) which is provided with a divided head. At (6) is a thin metal disk of the shape shown in separate sketch. This has carefully bevelled edges and is painted white. Periodically the disk is smoked over burning magnesium wire, so that the surface used is of white magnesium oxide. At (7) is a photometer track, carrying a movable incandescent lamp (8). The disk is connected by a belt with a direct-current series-wound motor in series with a variable resistance, and the same belt passes over the pulley of a Weston electric tachometer. At (9) is a piece of finely ground glass; at (10) a frosted bulb tungsten lamp, movable on a photometer track (11). At (12) may be placed diaphragms of any desired size.

For light source at (10) the requirements to be met were: first, as high intensity as possible; second, as white a source as possible, since prismatic dispersion and the selective absorption of the prism glass both decrease the amount of blue light for practicable slit-widths. A tungsten lamp burning at normal voltage was ultimately decided upon. At frequent intervals this was checked for colour upon a photometer by ascertaining the voltage to give the integral colour of three standards which were not burned at any other time. This proved fairly satisfactory, although some change in distribution undoubtedly occurred during the investigation, due partly to blackening of the bulb.

For light source at (8) carbon lamps were used, of uniform colour, ranging in candle-power from 65 to 5. These placed at various positions along the photometer bench permitted variations of illumination from 1 to 600 metre candles. The colour chosen was that of the incandescent lamp secondary standards at present in use, namely that of a 4·85 watts per mean spherical candle treated carbon, oval anchored filament. Use of an unsaturated colour of a particular hue will of course give results applying only to comparisons with such a standard. The complete study of the question will probably demand investigation of any possible effects of altering the character of the standard light.

The method of obtaining the luminosity curves is as follows:—The lamp (8) is placed to give a certain illumination; the disk (6) is turned so that the photometric field is bisected; the drum (5) is set at a point near the middle of the spectrum (taken always arbitrarily to give a mean wave-length of ·574μ); the divided head (4) is turned to give a slit-opening of 10 units (0·1 mm.): the lamp (10) is then moved until the two halves of the field are, as nearly as can be estimated, equally bright, at which point the lamp is fixed. A set of readings is then made, first by equality of brightness, then, with the disk rotating, by the flicker method, intensities being matched by changing the width of the slit (3). The wave-length drum is then changed to a point in the red, next to a point in the green or blue; and so alternating from one side of the original point to the other, similar double sets are made. When the whole spectrum as far as practicable is covered, a set of slit-widths is obtained, the reciprocals of which are as the brightnesses of the colours. By this means the illumination is constant throughout any one measurement —an important condition, which has been overlooked by several investigators.

Three sizes of field are used: one corresponding to the whole prism-face, an oblong 18 × 24 mm., somewhat larger, as viewed at 20 cm., than the angle subtended by the macula lutea; the second, a circular opening of 16 mm. diameter, subtending at a distance of 20 cm. an angle a little less than the macula lutea; the third, a circular opening of 6·5 mm. diameter, corresponding to the angular size of the fovea. At each illumination a set of equality of brightness and flicker measurements is made for each field-size. The making of such a set for one field-size consumes a morning or afternoon, and but one can be made safely in a day without unduly fatiguing the observer.

The measurements so obtained are subject to several corrections. These are: first, that for slit-width; second, that for prismatic dispersion; third, for the selective absorption of the prism; fourth, for the energy distribution of the source whose spectrum is used. The illumination as measured by the intensity and distance of the lamp (8) must be corrected for the loss by absorption through the telescope lens.

To determine the slit-width correction it is necessary to know the approximate luminosity curve and the portion of the spectrum included in each measurement. The latter was determined for the whole range of slit-widths used, and for the largest slit was found to amount to ·03 μ at ·66 μ, and to ·01 μ at ·49 μ. In the yellow, where the luminosity curve changes its direction most rapidly, the greatest width used is ·016 μ. In this region the correction calculated from the approximate luminosity curves is 0·6 of one per cent. This, the largest correction, is of the order of magnitude of the errors of observation, and may therefore be neglected.

The correction for prismatic dispersion was determined by measurements of the wave-length interval corresponding to the width of the eye-slit, using the drum divisions and spectral lines of known wave-length.

The correction for prism absorption and for energy distribution were determined together. Spectrophotometric comparison was made between the light of an incandescent lamp previously compared with a black body of known temperature, and the light of the tungsten lamp source through the ground glass (3) and the prism (2). Employing the Wien equation $J_\lambda = c_1\lambda^{-5}e^{-\frac{14500}{\lambda T}}$ to determine the energy distribution for the black body at the temperature measured, the distribution of energy from the source as used is given in fig. 11 (Pl. III.).

The calculated illuminations due to the various lamps placed on the photometric bench (7) are subject to a reduction of 10·5 per cent. as determined by measuring the absorption of the telescope lenses in a photometer.

A large number of observations of the character described were made almost daily during a period of about six months by the writer, and by other observers as will be noted. Illuminations were used whose corrected values are 1·8, 2·9, 8·9, 16·1, 26·9, 33, 68, 110, 175, 270 metre candles. These illuminations, because of the artificial pupillary aperture of 1 sq. mm., correspond to lower illuminations in practical photometry; they will therefore be referred to here as "illumination units."

The observations were plotted on thin, rather transparent coordinate paper, which permitted each observation to be compared with any other by simply superposing and holding to the light. This plan suited admirably; for in order to make all the comparisons necessary, each curve had to be studied in several different combinations. The same plan is of course impossible in publication, so that it will be necessary to select certain representative curves and to plot several in each diagram; the same curves will for that reason figure several times. The necessity for this will be evident from the following list of the combinations necessary for a complete comparison with one observer alone.

(1) *Effect of changing illumination, for each of three field-sizes.*

- (*a*) On the direct comparison curves.
- (*b*) On the flicker curves.
- (*c*) Relative position of the two curves due to the change.

(2) *Effect of changing size of field, at each of ten illuminations.*

  (*a*) On the direct comparison curves.
  (*b*) On the flicker curve.
  (*c*) The relative position of the two curves due to the change.

Among the curves are some showing bad points and some which, as the text indicates, do not exactly agree with those taken at other times. These imperfect curves (practically all "equality of brightness" curves) are used because even with their defects they show a proper relation to the preceding and following ones, while curves made at a later date purposely to replace them would correspond to a changed criterion. Attention must be called to the fact that in the measurements involving physiological variables, it is impossible to exactly reproduce conditions holding at one time ; hence data must occasionally be used for which, were it possible, one would by preference substitute other determinations. The curves selected have been most carefully chosen so as to represent most clearly the various phenomena brought out by the measurements.

Every effect to which attention is called and every conclusion is supported not only by the curves shown in this article, but also by others made at intermediate illuminations. Further, to avoid any possibility of error due to change in the light source between measurements, check settings at one time have been made to verify (at least qualitatively) those phenomena which are indicated by the differences between curves made on various days.

The data here presented consist principally of three sets :—

1st. Measurements made by the writer, chiefly during a period of about eight weeks in May, June, and July, 1910.

2nd. Measurements made by Mr. Luckiesh during July and August.

3rd. Measurements made at selected points for one field-size by five observers of normal colour vision during two weeks in September.

These will now be considered from various points of view. In turn will be taken up :

  (*a*) Relative sensibility of the flicker and equality of brightness methods.
  (*b*) Reproducibility of measurements.
  (*c*) Effect of changing illumination on each method for each field-size.

(*d*) Effect of changing field-size on each method, for various illuminations.

(*e*) The relative positions of the luminosity curves by the two methods at various illuminations and field-sizes.

(*f*) Comparison of luminosity curves obtained by different observers.

(*a*) *Sensibility.*

A measure of the relative sensibility of the two methods is obtained by taking the mean error of setting. In fig. 2 (Pl. III.) are plotted the mean errors for five observers at 250 illumination units for various points in the spectrum, from the deep red at $\cdot 66\,\mu$ to the green at $\cdot 51\,\mu$. The mean flicker errors are given by the full line, the mean equality of brightness errors by the dashed line. In fig. 3 are given the same quantities as obtained from observations at 10 illumination units. Several facts are here brought out clearly. First, the flicker method is for all parts of the spectrum several times as sensitive as the equality of brightness method at the higher illumination, the relative sensibility differing for different observers, but always favouring the flicker method. Second, the difference in sensibility between the methods is greater at high illuminations than at low. At the lower illumination the equality of brightness sensibility becomes greater, the flicker sensibility less. Third, the sensibility by the flicker method is less toward the ends of the spectrum, where the difference in hue between the spectrum colour and the standard lamp colour is greatest.

It is to be noted that while all five observers made readings by the flicker method which compared very closely to the accuracy of those made by the two most experienced observers (H.E.I. and M.L.) two of the others (by whom settings were made for the first time) averaged five or ten times the error by the equality of brightness method as by the other. This illustrates the great superiority of the flicker method as a method of measurement with observers not used to making matches between lights of widely different colour.

In connexion with the question of sensibility may be given the data on the speeds used with the flicker photometer. As is well known, sensibility varies with the speed, being less at high speeds. In fact, with high enough speed all flicker vanishes, no matter what the difference in illumination from the two sources under comparison. In these experiments the speed was always adjusted to the lowest value at which flicker could be made to disappear. This was then read by the tachometer and reduced to cycles per second. In fig. 4 (Pl. III.) are given the speeds as used by the different observers from end to end of the spectrum and for the two illuminations. The data show that much lower speed is necessary for low illumination, and that the ends of the spectrum require higher speed than the middle. These facts readily fit in with our knowledge derived from other sources and with such theory as we have of the action of the flicker photometer. The eye is more sensitive to flicker at high illumination than at low, hence the greater sensitiveness of the flicker method and the higher speed necessary at high illuminations. In order to compare lights of different colours it is necessary to attain such a speed that the colour flicker, due to difference in hue, disappears. It is therefore to be expected that at the ends of the spectrum where the hue is most different from the comparison lamp, a higher speed is necessary, and with this higher speed goes decreased sensibility. Whether the change in sensibility is exactly what the change in speed would occasion, or whether the change in speed is conditioned by hue difference alone, are points for future study.

In fig. 5 (Pl. III.) are plotted some preliminary data upon flicker speeds and sensibility under varied conditions of field-size and direction of vision. The two upper curves show the speeds (at 270 illumination units) for the largest and smallest fields used. The large field requires the higher speeds ; in other words, it is more sensitive to flicker. The lowest curve gives the speeds used for observation by peripheral or averted vision. To obtain these the smallest aperture was displaced to one end of the total available opening, and attention was fixed upon a small pin-hole (in which no flicker was visible) at the other end, about 8° distance, flicker being observed at the small aperture. The most striking feature is the much lower speed, corresponding to that required for lower illumination. Above are plotted the mean errors for observation by peripheral vision. These are much larger than by central vision. Later, the theoretical bearing of these points will be discussed. It is hoped ultimately to follow them up with more extended investigations of the retinal field, not only for speed and sensibility, but also for the character of the luminosity curves. These have, however, been deferred until some of the points of more direct interest to photometry are studied, although the complete explanation of the phenomena encountered will probably be brought out by study of extreme conditions, snch as those holding in peripheral vision.

(*b*) *Reproducibility of Measurements.*

Early in the course of the investigation a brief test of the reproducibility of measurements was made. It was then found that measurements made from day to day agreed to within the errors of measurement; that is, the individual flicker points agreed to within one to five per cent. depending on the part of the spectrum, while the equality of brightness points agreed somewhat less well. The chief object of the investigation at that time being to obtain knowledge of the relative positions of the two kinds of luminosity curves as simultaneously obtained, no further study of the question of reproducibility was made until the great body of curves here plotted were obtained.

At the conclusion of the measurements by the second observer (M.L.) the writer made a number of check measurements, which established a fact that had before been indicated by other occasional measurements, and by the measurements of M.L. This is that the equality of brightness curve may change its position with respect to the flicker curve in course of time. It appears that one's idea or criterion of a match in intensity by equality of brightness may change as compared with the flicker criterion, assuming the latter to remain fixed. Thus in the set of measurements given in Plate I. (Pl. IV.) the equality of brightness method showed, for large fields, the red less bright in proportion to the blue than did the flicker method. Three months later, after an interval of other work, the writer obtained, under the same conditions as before, curves with the red brighter by the equality of brightness method than by the flicker method; in other words, the equality of brightness curve had shifted from one side to the other of the flicker curve. The first curves of Plate I. and Plate V. (made on different lamps) show this change of relative position just described.

As to the amount of change experienced by each curve, the data as obtained do not give as complete an answer as is desirable, because some changes in the distribution of energy in the tungsten lamp took place in the interval of time, due to blackening, etc.; and in the last measurements an entirely new lamp had to be used. As the curves stand, they show slight changes in the flicker points, but very large in the equality of brightness ones. Taking into account the changes and differences in the lamps, it appears extremely probable that the flicker luminosity curve remains fixed to within the errors of measurement, while the equality of brightness curve remains fixed to within the errors of measurement only so long as one's memory retains the idea first formed as to the brightness of coloured fields. In course of time the latter curve may experience changes much greater than the change given by the errors of measurement.

A satisfactory test of reproducibility can only be made with lamps and apparatus standing absolutely unchanged between measurements—a condition which cannot be absolutely maintained. Nevertheless, a test approaching this in character has been carried out since the conclusion of the comparative measurements by different observers. Two seasoned "4-watt" carbon lamps have been used as sources, the apparatus has been clamped rigidly in position, and at intervals of about a week, for a period of two months, flicker and equality of brightness curves have been made by two observers. The middle-sized field was used, at the highest illumination (270 units).

In fig. 6 (Pl. III.) are plotted the mean deviations from the mean, or the mean error of setting, where the mean of all is taken as correct. These show less satisfactory reproducibility by the equality of brightness method than by the flicker method. The difference is not everywhere, however, as great as might be expected from the relative sensibility data and the considerations above mentioned. It must, however, be borne in mind that these results are obtained by two very practised observers, whose criterion of equality of brightness had become well fixed long before those measurements were made. With new observers or with observers who rarely made comparisons involving such large colour differences, the equality of brightness method would not have shown up so well. The indications are that with practice one's criterion becomes apparently fixed so that equality of brightness comparisons can be made with a high degree of reproducibility, though not with as high a degree as the flicker method. Whether this criterion is correct or not is another matter.

A point which deserves mention is the question of reproducibility at low illuminations. There it has been found by experience that reproducibility is much less satisfactory by both methods, and for a pretty clear reason, viz. one's illumination scale at low illumination is not a fixed but a shifting thing, due probably to the different physiological condition of the observer at different times. A set of curves for three field-sizes, for instance, will be obtained on three successive days and will show a certain relation at a given low illumination. After an interval of several days or any interruption of habits, an attempt to check these may give three curves consistent with themselves but corresponding either to a higher or lower illumination than the earlier curves. It is thus out of the question to ascribe a certain luminosity curve to a definite illumination, since the same illumination in metre candles corresponds at different times to different retinal conditions. Where then in the appended curves the illuminations are given for the low illumination observations, the figures indicate under what conditions the measurements were made, but do not necessarily mean that any one curve is only to be obtained at just that number of metre candles. The order of illumination is the important thing here, and the trend of the phenomena with changing illumination.

Work on the border-line between physiology and physics tends to shake one's faith in the principle of universal causation. Faith may be reconciled with experience only by constant reminder that however exactly physical conditions may be reproduced, one's physiological apparatus of seeing cannot be brought to a previous condition by any amount of careful work with metre stick or voltmeter.

These remarks on the shift of one's illumination scale apply only to illuminations of the order of twenty units and below; above that figure this difficulty disappears, and for that reason the reproducibility test described above was made at high illumination. Needless to say, the difficulties of low illumination measurements have necessitated close application and considerable repetition of work in order to secure the data presented.

(c) *Effect of changing illumination, on each method, for each field-size.*

In Plates I. and I. *a* (Pl. IV.) are given luminosity curves as obtained by the two observers by whom the complete sets of measurements (illumination and field-size varied) were made. These as plotted are corrected for prismatic dispersion, but not for the energy distribution of the source, and are arbitrarily made equal at ·574 μ. In the upper row are shown the curves obtained by the flicker method, four different illuminations being plotted together, in three groups, each representing one size of field. In the lower row the same data are given for the equality of brightness method. Appended keys indicate the illumination and field sizes in question.

From these curves it appears that the effect of change of illumination is to shift the luminosity curves along the spectrum. The most striking phenomenon is that while the shift with the equality of brightness method is toward the blue (Purkinje effect), the shift with the flicker method is toward the red, or exactly opposite. Also to be noted is that with the smallest field these shifts are less marked.

Examining the curves more in detail, several interesting points appear. Taking first Plate I. (H.E.I.) and examining the quality of brightness (lower) curves, it appears that the effect of decreasing illumination is two-fold: first occurs a broadening of the curves (increase of area), then an increase on the blue side, which results in a shift of the whole curve toward the blue. This may be interpreted as an increase on the red side, followed by an increase on the blue side, the latter becoming more marked at lower illuminations. With decrease in the size of the aperture these changes are much less, which is in accordance with the oft encountered statement that the Purkinje effect is absent for very small fields.

The flicker curves exhibit a plain shift toward the red, with not much difference for the different field-sizes until the lowest illumination is reached. At this lowest illumination there appears a drop on the red side, most marked for the largest field-size. In consequence of this the area of the curve is less and its maximum shifts again toward the blue.

Consulting Plate I.*a* we find the same general phenomena exhibited, a shift toward the blue for equality of brightness, toward the red for flicker, with decrease in illumination. Some differences between the results of the two observers are to be noted. Chief among these is that the corresponding changes in the curves take place at different illuminations and field-sizes from those of the first observer. The lowest measurement, for instance, was made at an illumination where the writer could secure no reliable flicker measurements.

As to the equality of brightness measurements, it is to be noted that the increase of luminosity on the red side of the curve is absent with the large aperture, slight with the middle aperture, and pronounced with the smallest aperture. The smaller increase of the blue sensitiveness or Purkinje effect with the small field is not only present, but because of the enhanced red sensitiveness the maximum of sensibility for low illuminations actually shifts toward the red, somewhat as the flicker curve for the same field-size and illumination. As a consequence of these facts the curves of this plate do not show a broadening of the curves, preceding the shift toward blue. The small aperture lowest-illumination curve seems to indicate a drop in red sensitiveness, or a reversal similar to the one occurring with the large field flicker curves with the writer. These secondary effects occur at the lowest illumination, where measurements are difficult, and thus cannot be established so well as the high illumination phenomena.

The flicker curves show similarly different effects due to changed illumination at different field-sizes, for while all show an increase of red sensitiveness for low illumination, the effect is most marked with the large field. There is no apparent reversal of the direction of the shift, although at the lowest illumination there is an increase of blue sensitiveness accompanying the increase of red, with the largest aperture. This is on a parallel with the drop in red sensitiveness at low illumination for large field in the writer's case.

One point is not well shown on these curves (which were selected to illustrate extreme cases), viz., that the shifts plotted occur chiefly at low illuminations. The high illumination curve represents very closely the position of the curves for a large range of illumination. Comparative fixity is found, in fact, from about 70 I.U. up.

The highest illumination (270 units) was the highest it was practicable to work at with the tungsten lamp. Some measurements made at about twice this illumination by viewing an acetylene flame directly showed that no appreciable change in the curves took place beyond this point.

(d) *Effect of changing field-size.*

Plates II. and II. *a* (Pl. IV.) present the luminosity curves at each illumination, as obtained with each size of field. The chief facts are, first, that at the high illuminations change of field-size has practically no effect on the flicker curves. Second, decreasing the size of field increases the red sensitiveness of the equality of brightness method (at practically all illuminations) but decreases the red sensitiveness by the flicker method. In other words, just as there is a reversed Purkinje effect, with the flicker method, so there is a reversed "yellow spot effect." In the case of this effect, as with the changes due to changed illumination, it was necessary for the second observer (Plate II. *a*) in order to experience these changes, to go to lower illuminations than did the first observer.

It is questionable whether the changes plotted in the high illumination curves for the equality of brightness methods are true "yellow spot effect" changes, or are due to the uncertainty of the method. Some check curves made two months after the first of Plate II., while exhibiting the same fixed character of the flicker curves, gave the equality of brightness curves as substantially the same for all field-sizes. There is, therefore, good ground for believing that at the highest illumination here used the effects of changing field-size are small or absent by both methods, although the inherent uncertainty of the equality of brightness method may indicate changes even at high illuminations. At lower illuminations the changes are of an entirely different order of magnitude from the uncertainties of judgment, and so can be described positively. It appears then that the Purkinje and yellow spot effects are two phases of the same low illumination phenomenon. In brief, at low illuminations for large fields there occurs the Purkinje effect by the equality of brightness method; the reversal effect by the flicker. At these illuminations a decrease in the size of the field decreases the effects.

(e) *Relative positions of flicker and equality of brightness curves.*

Plates III. and III. *a* (Pl. V.) give the relative positions of the two kinds of curves for three field-sizes and four illuminations. The most striking phenomenon is the large difference in the curves at low illuminations. At high illuminations the curves approach each other. In the case of the first observer, practical coincidence of the two curves is obtained for the middle-sized field at the highest illumination. In the case of the second observer (Plate III. *a*) this coincidence does not occur, the curves merely being much nearer together and (as test measurements at higher illuminations showed) they have reached a "steady state." With regard to the different relative behaviour of the two curves with the two observers, the remarks made on "reproducibility" and the comparative results of five observers given below, are *à propos*. With both the observers whose curves have so far been shown, there has occurred during the progress of the work a change of criterion with the equality of brightness measurements, and in the case of the five observers some show the equality of brightness maximum to one side, some to the other of the flicker. The only conclusions that can be drawn are that the two curves change from wide disagreement at low illuminations to a much closer agreement (in position of maximum) at high illuminations—the closeness of the agreement being difficult to determine because of the uncertainty in the real position of the equality of brightness curves. One point of significance is that although with both observers the two curves have reversed their relative positions on the red side, and in the comparative measurements by several observers the curves are differently placed on the red side, it has never happened that the flicker curve has shown more blue or green sensitiveness than the equality of brightness. In the writer's case, the two curves have been obtained exactly alike within the errors of measurement on two occasions, at two different high illuminations, with the middle-sized field, but this is as near as the blue part of the flicker curve has ever come to crossing over the other. Whether this would always be the case can only be determined by numerous measurements either extended over long intervals or by numerous observers.

It is possible that this phenomenon of lower green sensitiveness by the flicker method may be intimately connected with the fact that the comparison colour throughout was a yellowish white. Certain experiments not yet completed seem to indicate a dependence of the shape of the luminosity curve by equality of brightness on the colour of the comparison lamp. It has been found, for instance, that under certain conditions a spectrum yellow and a spectrum green may each appear by equality of brightness of the same intensity as a spectrum red, yet not appear equally bright when compared directly with each other. One might think, therefore, that a three-part field could be constructed in which two colours each appeared equally bright with the third, at their edges of contact with it, but not equally bright to each other at their common edge of contact. These phenomena of simultaneous contrast are yet to be investigated in connexion with the equality of brightness method, and the question must be settled as to whether any similar effects occur with the flicker photometer.

Perhaps the most interesting feature in these curves is their area. Casual inspection reveals the fact that the areas of the flicker and equality of brightness curves are frequently not the same. Now if the total light is the sum of the parts, this would mean the total light greater with one photometer than with the other. If the spectrum measured were that of a "4-watt" lamp exactly like that used as a standard of intensity, it would be possible to recombine the dispersed spectrum and make a homochromatic comparison of the two intensities of standard lamp and measured spectrum. This would of course be the same by both photometers. In other words, the physical summation must measure in this case the same, but by our curves the arithmetical summation is different by the two methods. One method or the other, perhaps both, must be deficient as judged by the ability to add or integrate the measured quantities. This question is being investigated further.

(f) *Comparative results obtained by different observers.*

When these measurements were finished it was thought well to obtain some measurements by other observers in order to serve as a check, and also to obtain data on differences to be expected between observers. Five observers in all were available, and these are indicated by initials. H.E.I. and M.L. are the two having previous experience with the apparatus ; P.W.C., no previous experience with apparatus, some experience in photometry, considerable experience in observing with various optical instruments ; F.E.C., long experience in photometry ; C.F.L., considerable experience with optical instruments and some in photometry. These observers have all perfectly normal colour vision. Before these measurements each observer made a number of settings with a three-colour mixing instrument (Ives' colorimeter) to match white. From these settings it appears that the observers differed from the mean by no more than 5 per cent. in the proportions of red, green, and blue necessary to make the match. Differences of this amount are found by the writer to be the rule with all who fall in the class of "normal vision." Those occasional observers who would be classed as partly colour blind will differ by forty or fifty per cent. from the writer or from the mean of several "normal observers."

Two illuminations were determined on, a high one of 250 units, a low one of 10 units, and the middle size of field was used. This choice of illumination and field-size was made in view of the previous work. The high illumination is one beyond which no changes in the relative positions of the curves are to be expected, the low illumination one at which flicker measurements are still easy to make. The middle size of field was chosen partly because it is the easiest one at which to make observations, and partly because the nearest coincidence of the two kinds of curves had been obtained for this size.

The apparatus was left undisturbed between experiments. Except in the case of the observers H.E.I. and M.L., the divided head on the slit was read by an assistant. The tungsten lamp was a new one which was given a short seasoning, and at the conclusion of the measurements its energy distribution was immediately measured, as before described.

Plate IV. (Pl. V.) exhibits the effects of changing illumination for the two methods, for each observer, with the mean curve of all. The chief phenomena of the previous measurements are here borne out. With the flicker method, decreased illumination increases the red luminosity; with the equality of brightness method the same change increases the blue luminosity (observer M.L. at this illumination shows merely a broadening of the curve). In the case of the less experienced observers the equality of brightness measurements are more or less wild, the flicker measurements very good.

Plate V. exhibits the relative positions of the two kinds of curves for each observer, with the mean. At the low illumination the equality of brightness curves are all higher on the blue side than are the flicker. At the high illumination two observers place the flicker maximum on the red side, two on the blue side of the equality of brightness maximum; one observer places the maxima about together, although, as has before been noted, the curves do not actually coincide, being of different areas.

The mean high illumination curves obtained by the two methods show close agreement in the position of the maxima, and it is not unreasonable to expect that with more observers or more observations extended over such an interval that the observers would not remember their previous equality of brightness criteria, the two mean curves would show practical agreement as to shape and position of maxima. On the other hand, it is apparent that an exact coincidence of the curves may not confidently be expected, but rather two curves of the same shape of slightly different areas.

Figs. 7, 8, 9, and 10 (Pl. III.) give the luminosity curves of all observers plotted together. It is obvious from these that even with workers of normal colour vision considerable differences may be expected (of the order of five to fifteen per cent.) in their measurement of pure colours against an unsaturated colour such as the light of an incandescent lamp. The observers maintain substantially the same relative positions with respect to each other, so that the different positions of their luminosity curves probably represent real differences in colour vision. The flicker curves lie closer together than the equality of brightness, so that in general the observers will differ less on their flicker measurements than on the others.

It is clear, however, from these curves that whichever method of measurement is employed, we cannot expect to obtain results in exact agreement from observers taken at random, where lights of different colour are to be compared.

The disagreement between observers will be less in comparing the unsaturated colours of any acceptable illuminants than in measuring bright spectral colours, but it is nevertheless evident that in establishing standards of different coloured lights, either the mean of a number of observers of "normal colour vision" must be taken, or the luminosity curve of each observer must be known in order that corrections may be made to his readings—when it is learned how to apply such corrections.

Fig. 11 shows the distribution of energy in the source used in the comparative measurements* (tungsten lamp through prism, &c.) and the mean flicker curve of five observers at 250 I.U. reduced to an equal energy distribution. Since the flicker curve closely agrees in shape with the equality of brightness curve, but is more definitely determined, it may be taken as the mean luminosity curve of these observers, and probably lies closer to being the luminosity curve of the normal or average eye than any heretofore obtained. Its maximum lies at $\cdot 545\,\mu$. This is in very good agreement with the high illumination curve obtained by Kœnig for his own eye†.

Summary of results.

The chief new experimental results of this investigation are :—

1. The flicker method is more sensitive than the equality of brightness method, where different coloured lights are compared.
2. The results by the flicker method are more reproducible than those by the equality of brightness.
3. Decrease of illumination shifts the maximum of luminosity toward the blue, by equality of brightness (Purkinje effect); toward the red by the flicker method.
4. Decrease of the size of the photometric fields at low illuminations shifts the maximum of luminosity toward the red for the equality of brightness method (yellow spot effect); toward the blue for the flicker method.
5. The relative positions of the two kinds of spectral luminosity curves are in general different.

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* The distribution of energy in the source used for Plates I. and II. (Pl. IV.) for an older tungsten lamp is slightly different from the lamp used in the comparative measurements.

† The value of $\cdot 565\,\mu$ for the maximum as obtained by Nutting for Kœnig's observations left out of account the correction for the dispersion of the prism.

6. The curves are most different in position at low illuminations with large fields; nearest together at high illuminations and with small fields. They may under certain conditions coincide, and the mean curves of several observers show close agreement in position of maxima and shape of the two curves at high illuminations, although the areas are not the same.
7. The curves obtained by different observers show different positions for each curve, and different relative positions of the two for high illuminations. At low illuminations all observers agree in showing the Purkinje and reversed Purkinje effects above described.

Theoretical Considerations.

No satisfactory theory of the action of the flicker photometer can be said to exist. What does it actually measure? We may assume the existence of a "luminosity sense" distinct from the colour sense. We may then form a geometrical picture of the alternations of luminosity as occurring in one plane, those of hue in another. In the second plane the sensations fuse more quickly, so that the sensation of flicker due to difference of luminosity persists longer than that due to difference in hue. Certain experiments by Tufts on the fatigued eye give some warrant for the assumption of this luminosity sense. The occurrence of colourless after images from coloured stimuli may also support this conception. The luminosity sense may be identified with the black-white element of Hering's theory. But at present it is questionable whether this luminosity sense can be considered as much more than a name used to assist in picturing the action of the flicker photometer. If it should be established that there does exist a separate "luminosity" element, which could be separated from hue by some photometric method, it would still remain to be established that this corresponded to our ordinary idea of brightness. If, for instance, there exists a physiological process called into action both by coloured and uncoloured light, a measure of this would be a measure of a common property. This might be satisfactorily termed "brightness" by a physiologist, but might not satisfy the photometrist who is interested not so much in the ultimate analysis as in things as they appear.

Dow has given reasons for believing the action of the flicker photometer to be chiefly ascribable to the retinal cones. The rods are known to be more sluggish, to possess greater inertia, so that they are less sensitive to flicker. The fact that the flicker photometer cannot be used at low illuminations, and that, as Dow found, the yellow spot and Purkinje effects are less by it, would support such a belief. The existence of a reversed Purkinje effect and a reversed yellow-spot effect, as found in the present investigation, appear to render Dow's theory inadequate. While a shift from cone to rod action explains very well the known facts of the Purkinje and yellow-spot effects and fits with the distribution of rods and cones in the retina, the flicker phenomena would appear to call for a more complicated mechanism of seeing.

Up to the present, the various facts upon which a more complete hypothesis may be formed are :—1st, The large increase in blue sensitiveness at low illuminations for large fields, and the smaller increase for small fields, by the equality of brightness method. 2nd, The large increase of red sensitiveness at low illuminations for large fields, and the smaller increase for small fields, by the flicker method. 3rd, The greater sensitiveness of the flicker method at high than at low illuminations, and for central as compared with peripheral vision. 4th, The complete failure of the flicker method at very low illuminations. 5th, The higher speed necessary for a large field centrally viewed as compared with a small field, and as compared with a small peripheral field.

Certain of these facts seem to support Dow's contention that the cones are probably the chief seat of action with the flicker photometer. The failure of the flicker method at low illuminations, where the rods are coming into play, speaks particularly for this. But it is necessary to ascribe some complexity of structure and behaviour to the cones if they are to suffice. As has been established by study of the retina, the cones are scarcer towards the periphery, but at the same time change in character, becoming larger. If we ascribe to these peripheral cones the property of exhibiting the typical cone characteristics (red sensitiveness and sensibility to flicker) more decidedly as the illumination decreases, we can account for some of the phenomena described above. In equality of brightness measurements such greater red sensitiveness in the cones would tend to compensate for the increasing activity of the rods and to preserve conditions of vision constant. If the flicker method uses only the cones, decreased illumination would bring out this compensating action at illuminations where the equality of brightness method would show comparatively little Purkinje effect, both retinal elements still being in action. As a matter of fact the curves of Plate IV. (Pl. V.) for five observers at an illumination of 10 units do exhibit, on the whole, a more marked shift toward red by the flicker method than is the shift toward blue by the other method. To explain the low sensibility and low critical speed for peripheral vision—an apparent reversal of the effect caused by increasing the size of the field—it is only necessary to assume the cones to be present in too small number, as the distance from the centre of the field becomes increasingly large, to play an important part. We then obtain rod flicker, which is produced by low speeds of alternation.

Along some such lines as this it is possible that the phenomena of the flicker photometer may ultimately receive explanation. The present work has not been carried sufficiently far into extreme conditions of illumination and localization upon the retina to establish that the action of the flicker photometer is to be ascribed chiefly to the cones, although this may appear probable. Even were this established there would still remain the larger part of the problem. For how do the cones fuse the colour impressions previous to fusing the "luminosity" impressions? Were the facts exactly opposite, if intensity flicker disappeared first with increased speed and colour flicker persisted, we could ascribe the luminosity phenomena to the rods or organs of colourless vision which possess greater inertia, and the colour phenomena to the cones, in accordance with the commonly known properties of each. Unfortunately, we must depend upon the cones for both the colour and flicker photometer phenomena; hence the need for ascribing to them some complexity of function as suggested above, and the difficulty of comprehending how the separation of luminosity and hue takes place.

Morris-Airey has suggested that the differences between the flicker and equality of brightness photometers may be ascribed to the different rates of the rise of sensation with different colours, a phenomenon which could affect the flicker but not the other instrument. For instance, in the flicker photometer, when adjusted to show no flicker, if either light source is obscured, the violently flickering illumination from the other source gives a decidedly greater impression of brightness than if the speed is increased until flicker disappears, or if one-half the steady radiation from that source is viewed. This apparently increased brightness has been found different for different colours. If this phenomenon is taking place even in the absence of all flicker, when the flicker photometer is at its mid-position, then the different amount of the effect for different colours might cause a difference in the readings of the photometers.

As yet this theory has not apparently received any thorough experimental test. It is not established that at the same illumination the rates of rise of sensation are actually different for different colours, and phenomena of this sort are extremely apt to be influenced by the order of the illumination. Nor is it established whether these phenomena are functions of speed rather than of the presence of noticeable flicker. In other words, whether the disappearance of flicker by alternation with another colour does not destroy these effects as completely as does the disappearance due to higher speed with the one colour. There is much yet to be investigated here, and in view of the differences between observers in their results as to the differences between the two methods, it is clear that these phenomena of rise of sensation must be studied with the same eye and apparatus by which are made the flicker measurements in which they may play a part.

And so it appears that there is no theory of the flicker photometer sufficiently supported by known phenomena to be at present satisfactory. The data collected in this investigation are probably insufficient to throw much light on the actual processes at work in the retina, and the investigation up to the present has had for chief object, apart from the practical photometric information so urgently needed, the location of landmarks from which to start the more searching investigations into the nature of the flicker phenomena and the brightness sensation.

Investigations which are now being carried on, or are planned with the same apparatus, are expected to furnish data which will assist in the formation of satisfactory theories. Prominent among these investigations may be mentioned: Luminosity curves as given by the method of critical frequency; the comparison of the physical and arithmetical summation of measured illuminations; the effect of changing the hue of the comparison source; the phenomena of rise of sensation as they occur in the flicker photometer as used; the connexion between hue difference, speed, and sensibility in the flicker photometer.

Bearing upon Practical Photometry.

The primary object of this investigation is to decide upon the photometric method and conditions to hold in determining the candle-power values of lights of different colours. Until the completion of the work laid down the full specification of these conditions cannot be made. There is as yet no answer to the question—What is the candle-power of a light in terms of a standard of different colour? Certain conclusions may, however, be drawn at the present stage of the work which will hold no matter what the final answer to the main question. One of these is that the sensibility and reproducibility of the flicker method are sufficiently greater than those of the other method to recommend its use in all cases where colour differences exist and where the question of absolute intensity values is not of the first importance. In the determination of distribution curves of a source, for example, a flicker photometer would be very convenient. A second conclusion is to be drawn from the comparative data by several observers of normal vision. From their differences of reading it is apparent that differences of colour vision will always be a serious obstacle to uniform results in heterochromatic photometry. The only practicable escape from this difficulty is to eliminate the need of making such comparisons in ordinary photometric practice; in other words, aim to make all practical photometry the photometry of lights of the same colour.

Under these conditions it is a matter of indifference what photometer is used, or whether the observer has normal colour vision. The problem of heterochromatic photometry hence becomes one for the standardizing laboratory, where secondary coloured standards or coloured glasses will be prepared for as many practical cases as possible. The search for a photometric method for coloured lights will in this work be treated from that standpoint.

Of considerable practical interest is the fact that the flicker method most nearly agrees with the method of equality of brightness at high illuminations. Until the problem is further toward solution it would appear well, whatever method is chosen, to make all heterochromatic comparisons at high illuminations. An idea of the order of magnitude of the illumination here meant may be obtained by noting that all the marked shifts (Purkinje phenomena, &c.) occur below 70 I.U. This corresponds to about 1/10 that number of metre candles as viewed by the normal sized pupil, or approximately, seven metre candles.

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Physical Laboratory,
National Electric Lamp Association,
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Table I.—Data for Plates i., ii., and iii. (Pls. IV. & V.)

The flicker luminosity curve for the 4½° field is reduced to the value unity at ·574 μ at each illumination, and the other data are given in terms of this. The data are corrected for dispersion, but not for the energy distribution of the source.

λ.	Field 8°·6 × 5°·16		Field 4°·58.		Field 1°·86.	
	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.
Illumination 270 Units.						
·657 μ	...	10·5	...	...	...	...
·565	14·3	...	14·2	11·5	13·3	13·3
·643	26·9	21·5	27·0	25·3	25·0	26·8
·632	42·9	38·8	42·3	41·7	42·0	43·7
·622	58·8	56·2	58·4	57·5	55·3	61·3
·6125	74·0	71·6	73·9	74·7	70·6	77·9
·593	98·4	98·8	96·0	97·8	98·4	97·1
·574	100·5	103·1	100·0	98·6	100·0	100·0
·555	89·0	96·8	92·1	92·6	91·1	93·3
·545	81·9	88·8	81·4	81·7	81·0	81·7
·535	66·8	74·3	66·0	67·2	66·5	69·3
·526	50·9	59·0	51·0	51·0	49·3	49·8
·517	34·3	36·1	33·0	32·7	32·0	32·4
Illumination 68 Units.						
·655 μ	...	...	14·0	17·4	15·2	...
·654	15·6	18·8	...	...	...	19·3
·642	30·4	30·7	29·0	31·1	30·4	34·4
·632	44·6	46·0	44·1	49·9	45·5	50·5
·622	59·6	60·3	59·1	65·4	59·6	65·3
·612	74·7	76·5	73·5	81·3	73·4	78·6
·593	98·3	95·2	95·0	100·5	93·9	99·6
·574	99·0	96·8	100·0	102·2	101·6	100·5
·555	87·8	93·2	89·8	96·3	88·3	91·2
·545	77·0	81·9	80·8	87·5	79·4	81·7
·535	64·5	70·6	67·9	74·7	66·6	69·2
·526	50·0	57·4	52·2	57·5	50·9	52·7
·517	33·3	37·7	35·5	37·4	31·5	32·0
Illumination 8·9 Units.						
·6525 μ	21·6	20·4	20·2	19·2	23·0	25·3
·642	37·6	34·4	35·4	37·4	37·9	43·8
·632	51·1	47·1	51·9	51·1	53·4	59·1
·622	71·1	68·4	65·8	69·0	68·6	80·1
·612	83·0	79·8	79·7	79·0	82·4	95·3
·593	101·6	94·5	101·6	101·5	102·8	116·7
·574	94·9	102·2	100·0	102·3	106·4	115·2
·555	84·2	103·9	87·9	108·8	93·4	101·1
·545	71·6	97·4	75·6	98·0	79·3	91·2
·535	58·1	90·3	61·0	88·2	67·0	78·9
·526	44·8	75·6	48·4	70·5	50·5	59·9
·517	27·7	54·3	30·9	50·1	31·6	40·1
·508	...	31·1	20·9	28·4	19·3	22·5

TABLE I. (*continued*).

λ.	Field 8°·6 × 5°·16.		Field 4°·58.		Field 1°·86.	
	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.
	Illumination 2·85 Units.					
·653 μ	20·2	14·2	20·9	17·5	22·6	23·2
·643	31·1	25·1	33·3	29·2	35·8	35·6
·632	48·5	43·7	48·7	44·9	49·6	48·1
·622	66·0	53·2	67·8	54·8	64·5	65·2
·612	75·4	65·2	80·3	68·9	78·4	77·5
·594	95·1	78·1	95·3	81·5	93·4	95·0
·574	95·9	85·9	100·0	90·6	95·9	93·7
·555	76·6	89·7	78·2	90·6	78·8	82·0
·545	66·8	86·6	66·1	83·2	71·3	76·6
·535	54·3	79·5	54·0	75·8	57·5	67·5
·526	39·2	62·0	37·5	61·6	45·9	54·3
·517	27·9	55·6	25·6	44·7	28·0	35·0
·5075	...	31·9	...	26·0	...	...

TABLE I*a*. Data for Plates I.*a*, II.*a*, and III.*a*.

The flicker luminosity curve for the 4½° field is reduced to the value unity at ·574μ at each illumination, and the other data are given in terms of this. The data are corrected for dispersion, but not for the energy distribution of the source.

λ.	Field 8°·6 × 5·16°.		Field 4°·58.		Field 1°·86.	
	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.
	Illumination 270 Units.					
·655 μ	14·0	12·0	13·4	12·9	13·1	12·7
·643	24·6	......	24·9	22·8	26·3	24·9
·632	38·5	38·8	41·3	38·8	41·8	40·1
·622	52·7	55·0	53·0	50·4	53·7	51·8
·612	68·9	64·8	68·2	62·7	67·5	65·7
·594	88·0	85·2	88·6	90·2	88·7	92·5
·574	100·4	99·2	100·0	100·8	98·5	105·4
·555	93·7	100·1	91·8	98·0	91·1	100·1
·545	83·0	87·0	82·7	91·4	81·8	89·1
·535	70·2	80·1	71·5	80·6	72·5	78·7
·526	52·9	62·9	55·4	65·8	53·5	61·4
·517	38·0	40·2	35·6	42·4	35·4	40·6

	Field 8°·6 × 5°·16.		Field 4°·58.		Field 1°·86.	
λ.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.
Illumination 8·9 Units.						
·653 μ	20·5	12·6	18·9	15·1	17·7	16·3
·643	35·2	19·4	32·8	25·9	33·3	30·8
·632	52·6	30·0	48·5	42·4	44·6	45·8
·622	66·4	42·6	65·8	54·7	59·7	59·2
·612	78·0	60·9	81·4	66·3	71·4	72·0
·594	97·6	87·2	96·4	90·1	91·1	97·0
·574	101·1	92·8	100·0	100·0	98·3	98·9
·555	90·5	97·7	90·6	96·8	91·1	96·3
·545	78·7	90·0	80·4	87·1	53·1	83·0
·535	63·5	79·5	65·7	81·2	66·9	75·6
·526	50·5	68·4	53·0	65·0	53·1	59·8
·517	33·2	49·3	33·8	43·9	34·9	41·3
Illumination 2·85 Units.						
·653 μ	...	11·4	26·1	14·1	21·5	20·9
·652	28·8	...	...	...	...	...
·643	...	20·0	...	...	...	...
·642	39·5	...	38·9	27·6	34·1	32·4
·632	58·7	32·8	53·7	37·0	48·3	46·4
·622	69·5	42·8	69·6	52·7	63·3	62·0
·612	84·4	56·6	75·8	65·4	76·7	75·8
·594	98·7	82·0	94·7	82·0	97·3	96·7
·574	101·2	89·0	100·0	95·3	98·8	101·2
·555	80·3	92·8	87·7	99·1	89·1	95·7
·545	75·6	85·1	72·1	88·6	79·4	89·4
·535	57·5	81 0	63·2	78·5	66·1	75·5
·526	48·0	61·7	50·9	66·5	52·7	62·2
·517	35·9	53·8	34·8	48·8	35·0	40 0
·5075	...	40·6	...	32·5	...	...
Illumination 1·25 Units.						
·655	...	6·69				
·653	...	...	23·0	14·0	21·6	20·5
·652	26·0	...	...	...	...	..
·643	...	13·9	...	...	...	...
·642	...	...	33·0	24·6	34·4	31·5
·6415	37·2	...	...	...	...	...
·6325	...	21·6	...	...	...	...
·632	...	...	48·2	37·0	53·8	46·8
·6315	57·3	...	...	...	...	...
·622	...	31·1	61·3	48·4	62·8	60·5
·6215	69·4	...	...	...	...	...
·612	77·7	39·4	72·2	57·6	75·3	67·9
·594	88·0	61·5	96·0	74·5	99·9	90·1
·574	83·8	71·3	100·0	88·6	101·7	107·0
·555	71·8	77·4	83·1	81·2	88·3	97·8
·545	60·2	78·5	66·3	85·0	77·6	88·0
·535	53·7	73·8	56·1	83·4	66·2	72·5
·526	44·1	70·9	47·1	66·8	48·8	61·3
·517	37·3	54·2	39·4	51·6	32·4	46·6
·508	.	...	...	42·5	...	29·1
·4975	...	...	...	25·5	...	...

TABLE II.—Data for Plates IV. and V. (Pl. V.) and figs. 7, 8, 9, and 10.

Given corrected for dispersion.

250 I.U.

λ.	H.E.I.		M.L.		P.W.C.		C.F.L.		F.E.C.		MEAN.	
	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.
·653 μ	16·3	18·5	16·3	12·6	25·6	31·2	22·7	46·3	19·4	38·8	20·0	27·3
·643	29·3	30·4	29·4	18·8	39·2	42·2	35·0	51·2	35·5	46·5	33·7	35·1
·632	42·4	46·4	39·1	32·6	52·9	63·8	46·6	85·5	45·8	52·6	45·3	53·5
·622	53·7	57·9	50·5	44·9	63·8	66·8	61·3	106·6	59·7	71·0	57·76	66·5
·612	66·2	73·5	62·9	58·1	74·8	80·0	70·1	75·8	70·2	70·0	68·75	68·9
·594	87·5	88·4	82·4	82·8	85·0	85·4	84·3	78·4	83·4	78·8	84·4	81·0
·574	91·0	90·5	90·9	93·1	84·7	86·9	85·5	67·1	84·1	89·4	87·21	85·3
·555	84·2	84·6	82·4	89·6	71·2	80·8	73·5	77·2	74·6	68·5	77·2	84·6
·545	73·5	75·9	74·4	81·2	62·6	72·6	65·4	63·5	64·8	59·9	68·0	72·6
·535	62·9	64·1	65·6	68·3	52·2	59·7	55·5	64·3	55·0	48·1	58·2	63·2
·526	50·8	50·8	53·5	58·6	38·6	49·1	41·7	43·0	41·4	31·0	45·2	48·4
·517	33·0	32·8	35·7	40·0	26·1	30·3	28·4	42·8	27·4	21·1	30·1	35·0

TABLE II*a*. Data for Plates IV. and V. (Pl. V.) and figs. 7, 8, 9, and 10.

Given corrected for dispersion.

10 I.U.

λ.	H.E.I.		M.L.		P.W.C.		C.F.L.		F.E.C.		MEAN.	
	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.	Flicker.	Eq. of B.
·653μ ……	19·5	16·6	18·7	11·5	29·1	29·5	26·6	39·0	29·2	27·2	24·6	24·9
·643 ……	33·8	29·5	30·4	25·2	42·2	42·0	40·4	65·7	40·1	39·4	37·4	40·4
·632 ……	47·9	43·2	45·9	39·3	57·7	60·2	56·6	82·0	56·5	58·3	52·9	56·4
·622 ……	64·6	57·4	59·3	50·7	71·7	70·1	68·9	102·8	68·5	60·0	66·6	68·2
·612 ……	75·6	69·2	72·2	63·3	84·8	83·2	80·0	99·3	81·6	76·2	78·8	78·2
·593 ……	90·1	87·8	92·8	87·1	92·0	92·0	92·8	114·0	93·8	92·8	92·3	94·7
·574 ……	92·7	90·6	94·3	93·0	86·3	92·6	88·6	96·2	86·9	93·5	89·7	93·2
·555 ……	79·9	85·2	83·0	90·4	71·4	81·9	72·7	135·2	72·1	87·6	75·8	96·1
·545 ……	67·9	77·8	74·0	83·4	62·6	78·0	60·9	125·0	63·5	81·2	65·8	89·1
·535 ……	56·4	68·7	61·5	73·7	50·0	71·5	49·2	65·5	52·8	71·0	54·0	70·1
·526 ……	43·8	54·5	48·5	60·0	35·1	56·8	36·7	108·8	40·5	54·6	40·9	66·9
·517 ……	27·3	37·1	31·4	43·5	24·4	38·7	26·6	69·5	26·0	44·4	27·1	48·6
·508 ……	19·0	23·0	21·0	26·9	……	24·3	……	28·2	……	……	20·0	25·6

Table III.

Mean Flicker Luminosity Curve for Five Observers.
Reduced to Equal Energy Spectrum.

λ.	
653	10·6
643	19·5
632	28·8
622	40·2
612	52·8
593	78·7
574	100·0
555	111·0
545	112·0
535	111·0
526	99·7
517	76·7

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XIII. *The Origin of the Small Bubbles of Froth.* *By* J. A. Pollock, *D.Sc., Professor of Physics in the University of Sydney* *.

[Plates VI.–VIII.]

I. *Introductory.*

WHEN a glass jar containing air and uncontaminated water is vigorously shaken, it will be found, immediately after the agitation, that air-bubbles have been formed in the liquid of comparatively large dimensions; these bubbles rise rapidly to the surface, but burst so quickly that there is only a momentary appearance of froth. With slightly concentrated solutions of many organic substances, or with water contaminated with a drop or two of insoluble oil, the result is strikingly different. In these cases small bubbles of various sizes, which are entirely absent when an uncontaminated liquid is used, are produced in great numbers. Some of the bubbles are so minute that they remain temporarily suspended in the liquid, while the larger ones, which appear almost immediately on the surface, constitute the most lasting part of the froth which is here such a characteristic outcome of the agitation. So numerous are the minute bubbles in many cases that they give a milky appearance to the liquid, thus forming with it a mixture which may conveniently be called an air, or gas, emulsion.

In referring to the question of the durability of liquid films, Lord Rayleigh † mentions Marangoni ‡ as the first, in 1871, to state in this connexion the necessary condition for stability. Subsequently, in 1878, the matter was independently discussed by Willard Gibbs §, who devotes, to the consideration of the general problem, a section of his famous Essay on the Equilibrium of Heterogeneous Substances.

To Lord Rayleigh we are not only indebted for an account of the frothing of liquids, contained in a lecture on "Foam," given at the Royal Institution in 1890||, but we also owe to him, as a result of his experimental researches in connexion

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* Communicated by the Author. From a paper read before the Royal Society of New South Wales.

† Lord Rayleigh, Proc. Roy. Soc. vol. xlvii., 1890; Scientific Papers, vol. iii. p. 341.

‡ Marangoni, *Nuovo Cimento*, vols. v., vi., 1871–2.

§ Gibbs, Trans. Conn. Acad. vol. iii. p. 467 (1878); Scientific Papers, vol. i. p. 300.

|| Lord Rayleigh, Proc. Roy. Inst. vol. xiii. 1890; Scientific Papers, vol. iii. p. 351.

with surface forces, the knowledge which affords a basis of fact to explanations advanced from theoretical considerations.

So far as I am aware, no explanation has yet been given why, with vigorous agitation, the bubbles are so much smaller and more numerous with a slightly concentrated solution than when a pure solvent is used, and it was to the discovery of the origin of these small bubbles that my own observations have been directed. The phenomenon is a striking one, and I feel that an explanation may have occurred to others, but no reference to its publication can be found.

Recently the matter of the frothing of solutions has become of importance in the mining industry in connexion with a floatation process for the concentration of ores; and I am indebted to Mr. H. Howard Greenway for a long list of organic substances which have been found to give a suitable froth, for the purpose of this method of concentration, when added in small quantity to water.

The list, which is, however, not put forward as exhaustive, includes organic acids, alcohols, ethereal salts, ketones, aldehydes, aromatic hydroxy compounds and essential oils, the substances being used, in the practical application, up to an amount which, in proportion to the water, is generally but a very small fraction of one per cent.

II. *Origin of the Small Bubbles.*

The froth is readily produced when gas under pressure is forced into the solution from the orifice of a pipe fixed vertically in the liquid, and for purposes of investigation this method of production is perhaps the most convenient one. With this arrangement, using a glass vessel to contain the solution, it is seen that the small bubbles are produced at the base of the main bubbles which are continuously being formed on the mouth of the pipe by the incoming gas. The inference is that the smaller bubbles are created from the newly formed surface separating the liquid from the mass of gas entering the solution, and instantaneous shadow photographs * of the bubbles, some of which are reproduced, in natural size, in Plates VI., VII., VIII., confirm this view.

Two classes of bubbles have, however, to be clearly distinguished: the one comprises those formed even when pure water is used, while the other class refers to the much smaller bubbles which are only created with a contaminated liquid, and constitute the characteristic feature of the lasting froth which is produced, in this case, by vigorous agitation. The necessity for the distinction may be recognized by comparing the companion photographs in Plates VI. and VII. Figure 2 of Plate VI. shows the breaking up of a large bubble of carbonic acid forced into uncontaminated water, while figure 3 exhibits the effect when a 0·1 per cent. aqueous solution of acetic acid is used, the conditions being, otherwise, the same in the two cases. Figures 4 and 5, Plate VII., are a similar pair of photographs with the pressure of the gas rather greater than in the former instance.

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* The photographs have been taken by the method described by Lord Rayleigh, Proc. Roy. Inst., vol. xiii. p. 261, Feb. 1891; Scientific Papers, vol. iii. p. 442.

The photographs show that the small bubbles of the froth of the acetic acid solution are the results of the disruption of the lower surface of the main bubble formed by the inrushing gas, the disintegration of the surface being extraordinarily great compared with the slight breaking up of the bubble, under similar conditions, in water.

It is interesting to find, from Whatmough's * measures of the surface tension of acetic acid solutions, that such a profound change, in the effect of the agitation of the water, is brought about by an alteration which only diminishes the surface tension, under isothermal conditions, by about 1·5 per cent. This effect is so small that, in any attempt to frame an explanation of the phenomenon, other factors, besides the mere change in the surface tension, must be taken into consideration.

For a solution to give a lasting froth the surface concentration must be greater than that of the mass of the liquid. From Lord Rayleigh's work it is known that on the production of a new surface in a solution capable of frothing, such as the surface of the main bubble in the present instance, the excess of concentration in the surface stratum is not instantly established, but requires time for its development. The extra concentration is produced as the result of molecular movement, and it is not to be expected that, while in the stage of growth, it will have, at any moment, the same value at all points of the newly formed surface. It must actually appear in the surface layer, in the first instance, in spots or patches; and wherever such a patch of extra concentration is formed the surface tension becomes, as a necessary consequence, less than that of the surrounding parts. The conditions here are not isothermal ones, and the lowering of the tension may be greater than that mentioned above. The newly formed

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* Whatmough, *Zeit. für Phys. Chem.* vol. xxxix. p. 166 (1902).

bubble is thus, with reference to its surface tension, for a time at least, essentially uneven in texture, and to this fact, no doubt, the disruption of the surface is mainly due.

The characteristic small bubbles of the froth are only formed when the mass of incoming gas possesses considerable downward momentum. In this case the pressure on the base of the main bubble is high, and as the conditions are anything but those of equilibrium, the liquid underneath is being strongly accelerated. The consequent disruption of the surface, as shown in the photographs, is so complete, that its development cannot be followed in detail, but a not improbable idea of the production of the small bubbles may be formed by considering that the patches of extra concentration on the base of the main bubble, as they offer, at the moment of their appearance, slightly less resistance than the rest of the surface, yield more to the impact of the gas; in the general violent movement the patches may thus get blown out from the bubble before other adjustment of the surface takes place, and appearing first as cylindrical protuberances, finally become completely detached, owing to the well-known instability of cylinders, in this connexion, when their length exceeds the circumference.

In the case of oil-contaminated water, the first result of agitation will be the dissemination of minute drops of oil throughout the liquid. On coming into contact with large bubbles, these drops will spread out on the surfaces into patches, thus establishing that weakening of the surface tension in spots, which, according to the description just given, is, under highly kinetic conditions, but the preliminary to the disruption of the surfaces. Such an origin would ensure to the small bubbles that layer of contamination essential for their stability, and the explanation of their production here suggested would thus account for their uniform durability.

Owing to the circumstances of the development, the exact manner of the creation of these small bubbles must remain a matter of some conjecture, and the foregoing description is put forward in no other sense. The surprising feature, which requires explanation, is the fact that the addition to a solvent, which alters the effect of its agitation from a few evanescent bubbles to a dense lasting froth, may involve, in the value of the surface tension, a diminution, under isothermal conditions, of only about one per cent., an amount altogether too small, if taken by itself, to be considered as changing the conditions.

The small bubbles, here under review, are characteristic of the froth which is produced by violent agitation, and are not dependent on the method which is used for introducing the gas into the liquid. It is considered that, in all cases, they are the results of the disintegration of the surfaces of larger bubbles, the essential condition for their creation being the development, on these surfaces, of spots of diminished surface tension, associated with a gas pressure within the bubbles considerably in excess of that required for equilibrium in the circumstances existing at the moment of disruption.

It yet remains to consider the production of the bubbles formed by processes which are independent of the nature of the liquid used, such as those which result from the breaking up of a jet of gas when forced into uncontaminated water, or into a solution which does not yield a lasting froth. In these case, as may be seen by a comparison of the photographs, the bubbles belong, as a whole, to a much larger class than those in the acetic acid solution whose origin has just been considered.

The larger of the bubbles of the class now under discussion are created by the partition of the volume of gas entering the liquid, considerable portions of the gas being "pinched off," as it were, by the action of currents in the liquid, or, having lost their downward momentum, becoming separated from the mass of inrushing gas owing to their buoyancy. Bubbles made in some such way are always created when a liquid of any kind is agitated, and the class includes the largest of the bubbles which are produced by any method of disturbance.

But there are other bubbles of the same general class, though much smaller, whose development follows a more orderly course. These are shown in various stages of their growth in the photographs of Plate VIII., the reference being to bubbles from about a tenth to a few millimetres in diameter in many cases still attached to the parent surfaces.

Figure 6, Plate VIII. shows clearly two of the bubbles in an early stage of development, still part of the lower surface of the bubble caused by a jet of carbonic acid entering a 0·1 per cent. aqueous solution of acetic acid, the pressure of the gas being too low to cause the disintegration of the surface of the main bubble. Figure 7 is a photograph of a bubble of carbonic acid being formed in water, and figure 8 one of a bubble of the same gas in a 0·1 per cent. aqueous solution of sulphuric acid.

Whatmough * shows that dilute aqueous solutions of

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* Whatmough, *loc. cit.*

sulphuric acid have a surface tension which *increases* as the concentration becomes greater; they may be said, then, to lack the frothing property even more than water. The acetic acid solution has a surface tension which *decreases* as the concentration increases, so the photographs of Plate VIII. may be taken as exhibiting the bubbles in three typical liquids, and, by showing the similarity of the detail in the three cases, proving a common method of production.

Here the development, previously suggested as that of the small bubbles of froth, is clearly apparent; cylindrical protuberances are formed on the larger surfaces which lengthen until the state of instability is reached, they then become detached as separate bubbles.

In seeking for an explanation to account for these protrusions into the liquid of the surfaces of the gas bubbles, any consideration of a local weakening of the surface tension seems here out of the question. Firstly, a cause is not apparent for an accidental diminution of the surface tension in somewhat large patches, confined within narrow limits as to size; secondly, the effect is shown both with tap and distilled water, used with every precaution to avoid contamination, and no difference occurs when the gas is carefully filtered: moreover, bubbles of the class under consideration, produced in water and in non-frothing solutions, show no special durability. That the phenomenon is not directly dependent on any directed momentum of the gas is proved by the fact that in the photographs the projections are shown on the surface of closed bubbles, in which the gas can have little, if any, general momentum relative to any part of the surface.

The outline in the photographs is fairly sharp as the exposure was of the order of a millionth of a second, but in each case the liquid was in a state of considerable turbulence. With this fact in view, it is suggested that the bubbles, whose development is shown, owe their origin to variations in the external pressure on the parent surfaces due to the motion of the liquid relative to these parts of the larger bubbles. In this case the size and number of the bubbles will depend on circumstances which determine the nature of the liquid movement.

This suggestion as to the origin of these small bubbles is prompted by the result of the process of exclusion previously outlined, and though impossible to prove, as the turbulence of the liquid cannot be directly seen, is not improbable from the appearance of the detail shown.

III. *Summary.*

The object of the investigation was to find the origin of the small bubbles which constitute the characteristic feature of the froth which is produced by violent agitation. The froth is readily created when gas under pressure is forced into a liquid through the orifice of a vertical pipe; and in order to study the conditions of its formation, instantaneous shadow photographs have been taken of the jet of gas in various solutions. It is seen from an inspection of the photographs, that the bubbles which result from the breaking up of the jet may be separated, with respect to the exact manner of their production, into three classes.

1. Large bubbles are created by the partition of the main bubble which is being continuously formed on the end of the pipe, considerable portions of the gas being "pinched off," as it were, by the action of currents in the liquid, or, having lost their downward momentum, becoming separated from the mass of incoming gas owing to their buoyancy.

2. The photographs accompanying the paper show small bubbles which are clearly the result of the detachment of cylindrical protuberances formed on the surfaces of the larger bubbles, the protuberances having lengthened until the state of instability has been reached. These bubbles are seen in various stages of their attachment to the parent surfaces, and are shown to occur in water, and in a non-frothing as well as in a frothing solution. It is considered that the typical protuberances, from which the bubbles develop, owe their origin to variations in the external pressure on the parent surfaces, due to the motion of the liquid relative to those parts of the larger bubbles.

3. Finally, there are bubbles, on the whole smaller still, which occur only in cases of the violent agitation of oil-contaminated liquids, or of solutions capable of frothing. These are, indeed, the characteristic bubbles of the froth which is produced in these circumstances. With the special method of agitation which was used in this investigation, these bubbles are shown to be due to the disruption of the lower surface of the main bubble formed by the gas entering the liquid, the disintegration of the surface, in a 0·1 per cent. aqueous solution of acetic acid, being seen to be extraordinarily great compared with the slight breaking up of the bubble, under similar conditions, in water. The surprising feature in connexion with the occurrence of these bubbles is the fact that the addition to a solvent, which changes the effect of its agitation from a few evanescent bubbles to a

dense lasting froth, may involve, in the value of the surface tension, a diminution, under isothermal conditions, of only about one per cent. The suggestion is made that the disruption of the surface, which results in the small bubbles, is due to a high gas pressure associated with a weakening of the surface tension in small patches, which may occur in a newly formed surface while the surface concentration is acquiring its full value, or in the case of an oil-contaminated liquid, may be caused by the appearance of small oil spots on the surfaces of large bubbles, resulting from the contact of the bubbles with minute drops of oil disseminated, by the agitation, throughout the liquid.

XIV. *Note on the Application of Thermodynamics to the Discharge of Electricity by Hot Bodies. By* Prof. H. A. Wilson, *F.R.S., McGill University, Montreal* [*].

In 1903 the writer published a calculation of the current carried by the ions emitted by a hot body as a function of the temperature based on thermodynamical reasoning [†]. The result obtained may be expressed in the following form :

$$p = A\theta^{(1+a/R)}\epsilon^{-w_0/R\theta}, \quad . \quad . \quad . \quad . \quad , \quad (1)$$

where p is the equilibrium pressure due to the ions emitted at absolute temperature θ, R the gas constant, A a constant, and w the work required for an ion to escape is supposed given by the expression

$$w = w_0 + a\theta$$

where a is a constant. According to this the form of the function p depends on the value of the constant a.

In a recent number of the Philosophical Magazine Prof. O. W. Richardson [‡] has given a similar calculation of p as a function of θ, but has come to the conclusion that the form of the function is unaltered when w instead of being constant is a linear function of the temperature.

The difference between the two conclusions is due to the fact that Prof. Richardson has neglected a term in his equations which is only negligible when the constant a has a particular value.

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[*] Communicated by the Author.

[†] Phil. Trans. A. vol. ccii. pp. 243–275.

[‡] Phil. Mag. April 1912.

Richardson finds (page 603)

$$\frac{w}{\theta}-\frac{w'}{\theta'}+\mathrm{R}\left\{\log\frac{p}{p'}-\frac{\gamma}{\gamma-1}\log\frac{\theta}{\theta'}\right\}+e\int_{\theta'}^{\theta}\frac{\sigma}{\theta}\,d\theta=0, \quad . \quad (2)$$

in which I have corrected obvious misprints, and (page 605)

$$\sigma=\frac{1}{e}\left\{\frac{\mathrm{R}}{\gamma-1}-\frac{dw}{d\theta}\right\}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If $w=w_0+a\theta$ equation (3) gives

$$e\int_{\theta'}^{\theta}\frac{\sigma d\theta}{\theta}=\left(\frac{\mathrm{R}}{\gamma-1}-a\right)\log\frac{\theta}{\theta'};$$

and with this (2) becomes

$$w_0\left(\frac{1}{\theta}-\frac{1}{\theta'}\right)+\mathrm{R}\log\frac{p}{p'}-\mathrm{R}\left(1+\frac{a}{\mathrm{R}}\right)\log\frac{\theta}{\theta'}=0. \quad . \quad (4)$$

This is the same thing as (1), the result which I obtained.

Prof. Richardson neglects the term $e\int_{\theta'}^{\theta}\frac{\sigma}{\theta}d\theta$ in (2), which of course is only permissible when σ is very small, so that from (3)

$$\frac{dw}{d\theta}=a=\frac{\mathrm{R}}{\gamma-1}.$$

Unless this particular value of a is used we do not obtain

$$p=\mathrm{A}\theta^{\frac{\gamma}{\gamma-1}}\epsilon^{-w/\mathrm{R}\theta},$$

which is the equation from which Richardson draws the conclusion that the form of the function is independent of the value of a.

It appears therefore that the expression I obtained is in reality confirmed by Richardson's method of calculation when the integral term is not omitted.

XV. δ *Rays.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper read before the Royal Society [*], I described some experiments whose object was to test whether an electron ejected by an α particle has a component of motion in the direction in which the α particle is moving. The experiment consisted in measuring the ionization produced by collision between an aluminium plate and a parallel sheet of aluminium foil through which α particles were projected on to the aluminium plate. It was found that the "collision" leak was always greater when the foil was at a negative potential in comparison with the plate than when it was at a positive potential. From these experiments I concluded that the ejected electrons have a component of motion of the nature aforesaid.

Dr. Campbell has recently described some experiments in several papers to the Philosophical Magazine [†], in which, using a similar arrangement, he measured the number of electrons given off from the metal surfaces where the α particles emerge, and where they enter (no ions being produced by collision), and found no difference in the numbers in the two cases. He therefore concluded that the ejected electron has on the average no component of motion in the direction of that of the ionizing α particle.

In my paper I stated that probably the gas itself plays directly only a small part in the production of this asymmetry. This is, however, not the case, as I will now show. In order to explain what happens in the gas I must refer to a previous paper [‡]. It is there pointed out that the nature of an ion cluster in a gas at constant temperature is not constant, as is usually supposed, but is constantly going through a cycle of changes. These changes are similar in character to the chemical changes going on in a partly dissociated gas, and are regulated by the same laws, namely, the laws of thermodynamics and the law of mass action. The free ion and every ion cluster has, therefore, an average period of life before becoming a cluster of a different nature. This property of the ion must play an important part in the production of ions by collision. Thus, consider a number of ions in a gas not under an electric field. At any instant there are a certain number of free ions and clusters of various complexities in the gas. Suppose the gas now subjected to an electric field just sufficiently strong to produce ionizations by collision of the negative ions. The field will seize upon each free electron and give to it as it passes over its mean free path a velocity sufficient to produce ionization by collision. But the velocity given to the clusters in the gas would not be sufficiently large to produce ionization by collision. When, however, the electron forming the nuclei of a cluster becomes free, which occurs at the end of its period of life, it is at once seized upon by the electric field, and ionization by collision is produced in the same way as before.

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[*] Proc. Roy. Soc. A. vol. lxxxiii. p. 195 (1910).

[†] Aug. 1911, p. 276; Jan. 1912, p. 46; April 1912, p. 463.

[‡] Proc. Camb. Phil. Soc. xvi. pt. iv. p. 285.

Since the period of life of a cluster depends on the nature &c. of its collision with the molecules of the gas, it will be affected by the electric field when the velocity given to the cluster by the field becomes comparable to its velocity of translation. An increase in the field would then produce a decrease in its period of life.

Let us now return to the discussion of the experiments mentioned. Suppose the electric field in a gas is parallel to the direction of propagation of the stream of ionizing α particles, and that each electron ejected by an α particle has a component of motion in the same direction as the α particle is moving. Firstly, let us suppose that the direction of the electric field is such as to give a motion to the electron in the same direction as its initial motion. The field will seize upon the electron, and it may have a sufficient velocity given to it before it strikes another molecule to be able to produce ionization by collision. Suppose now that the field is reversed. The field will then have to reduce the electron to rest first before a velocity in the direction of the field can be given to it. But when the electron has little or no velocity it is very liable to attach itself to a neutral molecule. The cluster produced would then have to run a distance A (which depends on its velocity and period of life) before the electron becomes free, after which it is seized upon by the electric field, and possibly ionization by collision produced. The conditions for the production of ionization by collision are therefore less favourable in the latter case than in the former, owing to the ejected electron forming a cluster more readily in the latter case. The effect produced is roughly as if we were to suppose the electron ejected in all directions by the α particle, but the distance between the electrodes decreased by A in the latter case.

It should also be pointed out that when the electric field is in such a direction as to give to the electron a motion in the opposite direction to its initial motion, its chance of recombining with its parent molecule is greater than when the field is in the opposite direction. This would give rise to an asymmetry in the collision leaks in the same direction as the effect just considered.

A simple consideration will show that the asymmetry should increase with the distance of separation of the plate and foil. The collision leak due to the ionization of a slab of gas of thickness dx midway between the electrodes is equal to $Ce^{\frac{x}{2}\alpha}$ when the field is in one direction, and roughly $Ce^{\left(\frac{x}{2}-\text{A}\right)\alpha}$ when the field is reversed, using the usual notation. The difference between the leaks thus rapidly increases with x, the distance between the electrodes. It would also depend on the nature and pressure of the gas. The asymmetry may thus be very large under favourable conditions. I found, for example, in one of my experiments when the chamber contained hydrogen at a pressure of ·8 cm. of mercury, that the leak changed from 928 to 1592 on reversing the field, the difference of potential between the electrodes, which were separated by ·5 cm., being equal to 490 volts. Dr. Campbell has informed me, in a private letter, that he also gets a great change in the magnitude of the leaks on reversing the field when it is very large. He finds it especially noticeable when the field is so large that the positive ions produce ions by collision. This fits in with what we would expect from the foregoing considerations. Any effect that increases the magnitude of the collision leak increases the asymmetry. Now the leak is greatly increased when ionization by collision of the positive ions begins to come in. It is equivalent to supposing that a sudden increase in the value of α takes place, which, as shown by the expression given, would produce a great increase in the difference between the leaks.

The question now arises why there appears to be no appreciable difference in the number of electrons given off from the incident and emergent surfaces of the electrodes. If the component velocity of the electron in the same direction as the motion of the α particle is small, the effect may easily be masked by the various disturbing effects which exist. Thus my experiments and Dr. Campbell's suffer in this connexion from two defects, which are, however, unavoidable. In order to use as large a number of α particles as possible a beam is used in which the α particles are not parallel to one another. Now it can be shown than when an

α particle enters and leaves a metal surface at an angle of 45°, the asymmetry in the number of electrons given off would be about one half that when the angle is equal to 90°. Such an arrangement thus decreases the asymmetry. Further, it is known that the number of ions or δ rays made along the path of the α particle increases as the velocity of the α particle decreases. Thus the number of δ rays produced in the surface layer of the electrode where the α particles emerge is less than in the layer of the same thickness where it enters. This produces an asymmetry in the opposite direction to that which would be produced if the electrons ejected have a component of motion in the same direction as the motion of the α particle ; and may thus largely eliminate the asymmetry due to the latter cause. The foregoing effects in conjunction with the volta effect and other disturbing causes may render the asymmetry uncertain in magnitude and sign.

It should be noticed that the ejected electron must have a velocity sufficient to carry it out of the sphere of influence of the positively charged parent molecule, otherwise the two will at once combine again. If its velocity is zero when out of the influence of the parent molecule, practically no asymmetry would exist in the number of electrons given off from the incident and emergent surfaces of the electrodes when a steady state has been reached, for the electrons could reach the surface by diffusion only in each case. But the collision leak would show an asymmetry in the way explained.

It appears, therefore, that more reliance must be placed on what happens in the gas between the electrodes than what happens on their surfaces. I maintain, therefore, that my experiments indicate that the electron ejected by an α particle from a molecule has a component of motion in the same direction as the motion of the α particle. There does not seem to be an alternative explanation of the experimental results. If they are due to an asymmetry in the number of electrons from the metal surfaces, they indicate the same property. If they are due to an asymmetry in the number of positive ions given off by the metal surfaces, they would again indicate the same property. The positive part of the molecule on being ionized would, in this case, be given a motion in the opposite direction to the motion of the α particle. But this is equivalent to giving the electron a motion in the same direction as the motion of the α particle.

Yours faithfully,

R. D. Kleeman.

XVI. *Notices respecting New Books.*

Conic Sections by the Methods of Coordinate Geometry. By CHARLES SMITH, *M.A.* New Edition, revised and enlarged. Macmillan & Co.: London, 1910.

Elements of Analytical Geometry. By Prof. G. A. GIBSON and Dr. P. PINKERTON. Macmillan & Co.: London, 1911.

Coordinate Geometry of Three Dimensions. By R. J. T. BELL, *M.A.*, *B.Sc.* Macmillan & Co.: London, 1911.

THESE admirable books are all of the nature of elementary treatises, intended for students beginning the study of coordinate geometry. Mr. Smith's treatise has long held its place as a thoroughly sound and well-planned text-book; and in its latest form will no doubt commend itself to a still wider circle of eager students. Among the additions to the new edition is a short chapter on Invariants.

The text-book written by Professor Gibson and Dr. Pinkerton is somewhat more elementary than the first named, but covers a wider field. The straight line, circle, and conic sections generally are treated separately; but other curves are considered. One special feature of the book is the great number of excellent diagrams drawn on squared paper. These cannot fail to be of great instructive value to the pupil. Another excellent feature is the early introduction of what Chrystal called the "freedom equation" of a curve, in which x and y, instead of being expressed in terms of one another, are each expressed in terms of a third variable. The method is known in some books as the parametric representation; but there is no doubt that Chrystal's distinction between the Freedom and the Constraint equations is one that should be early brought to the mind of the student, and the phraseology is particularly happy.

Mr. Bell, in his treatise on surfaces and lines in space, makes good use of the Freedom equations; and it is a pity that he missed the opportunity of calling them by this picturesque title. Why do not geometers describe the relation among the coordinate axes in terms of right-handed screw motion, instead of defining the relation in terms of counter-clockwise motion? Why not clockwise? naturally asks the youthful critic. But there can be no criticism when he is told that forward motion along the x-axis is to be combined with right-handed motion round that axis as we pass from the y-axis to the z-axis, and so cyclically through the set. Once the student gets this simple cork-screw idea into his head he has never any difficulty in laying down his axes in space. Throughout the book the author uses the old-fashioned expression, "equation to" a curve or surface, instead of the more usual "equation of." These, however, are trifling matters in comparison with the general excellence of the book.

All three treatises abound in numerous examples and are models of mathematical printing.

XVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from Vol. xxii. p. 820.]

June 14th, 1911.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'On a Monchiquite Intrusion in the Old Red Sandstone of Monmouthshire.' By Prof. William S. Boulton, B.Sc., Assoc.R.S.C., F.G.S.

The paper describes a hitherto unrecorded monchiquite, intruded into the Upper Old Red formation of Monmouthshire, about midway between Chepstow and Usk. The precise manner of its intrusion is doubtful; reasons are given for regarding it either as a dyke with a north-westerly trend or as a volcanic plug (bysmalith). The disturbance and metamorphism of the contact-rocks (seen only at its eastern edge) are dealt with, as also the rounded lumps of marl and subangular blocks and chips of sandstone incorporated in the igneous rock.

The monchiquite, which is described in detail, contains unusually large phenocrysts (measuring up to 5 and 6 inches) of augite (chrome-diopside) and biotite, generally much corroded. Rounded lumps or 'nodules' of olivine-augite rock with chromite are also included, the olivine now being represented by secondary products, including iddingsite. A second generation of purple idiomorphic augite, biotite, and decomposed olivine occurs porphyritically in the ground-mass, with occasional granules of quartz and chromite.

The ground-mass is a felt of minute elongated augite-prisms, magnetite-grains, and flakes of biotite, and the remaining space is occupied by analcite enclosing apatite-needles. Reasons are adduced for regarding the analcite of the ground-mass as primary. Ocelli filled with secondary carbonate, chlorite, analcite, etc. are common.

A complete analysis of the rock is given, which bears out the petrographical evidence that it is a very basic lamprophyre belonging to the monchiquite group. It is compared with other rocks of the group, and in particular with the monchiquites and camptonites of Colonsay, with which it has many points in common. Finally, its age and possible connexion with the only other known intrusion into the Old Red Sandstone of the South Wales area—that of Bartestree, near Hereford—are referred to.

2. 'Notes on the Culm of South Devon: Part I.—Exeter District.' By Frederick George Collins, F.G.S.; with a Report on the Plant-Remains by E. A. Newell Arber, M.A., F.G.S., and Notes on the Cephalopoda, by George C. Crick, Assoc.R.S.M., F.G.S.

November 8th, 1911.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

The following communications were read :—

1. 'On the Interglacial Gravel-Beds of the Isle of Wight and the South of England, and the Conditions of their Formation.' By Prof. Edward Hull, M.A., LL.D., F.R.S., F.G.S.

The author, after referring to the investigations of previous authors, especially of Mr. Codrington and the officers of the Geological Survey, with which he in the main agrees, points out that the origin and mode of formation of the gravel-terraces of the Isle of Wight and the New Forest districts are still open to discussion. He points out that the levels of the higher beds on both sides of the Solent up to about 400 feet indicate the amount of subsidence of the whole area at a time when the stratified gravels, composed mainly of rolled flints, were formed at the margin of the uprising ridges of the Chalk in the post-Glacial Epoch, for this part of England. Preceding this was the great uplift indicated by Godwin-Austen, by which the British Isles were joined to the Continent as land. By this uplift the British Channel was laid dry, and along its centre there ran a river from its source about the Straits of Dover to its outlet into the ocean through the Continental Platform. This river-channel is laid down on the Admiralty Charts under the name of 'the Hurd Deep' for a distance of 30 miles of its course, and has been named by the author 'the English Channel River.' The author considers the gravel-beds of this district to be the representatives of the High-level Gravels of the Midlands and Cromer, also of the 'Interglacial Gravels' of Cheshire and Lancashire, and the shell-bearing beds of the Denbighshire Hills, and of Moel Tryfaen in Wales, at levels of about 1200 feet above the sea.

2. 'The Gopeng Beds of Kinta (Federated Malay States).' By John Brooke Scrivenor, M.A., F.G.S.

The paper as originally presented was the outcome of field-work done chiefly in 1910; but, as it had to be held over until the November session, an appendix has been added giving additional evidence supporting the author's views and more information about the extent of the Gopeng Beds.

Gopeng is a prosperous mining centre in the Kinta Valley, close to the granite of the Main Range of the Malay Peninsula. The following is the succession of the rocks :—

YOUNGEST	The Mesozoic granite, with its modifications and veins.
	Phyllites and quartzites.
	The Gopeng Beds.
OLDEST	Crystalline limestone (Carboniferous or Permo-Carboniferous).

The physical features of the country are described, and it is shown that not only are the Gopeng Beds cut by veins from the granite and altered at the junction with the granite, but they are also faulted down against the limestone, which forms precipitous hills.

The Gopeng Beds, consisting of clays and boulder-clays with some stratified drift, are of glacial origin. This is proved by the inclusion of large boulders in the clay, by the physical condition of the components of the clays and their distribution, and by the striking resemblance of the beds as a whole to Pleistocene glacial detritus.

The nature of the beds is considered to be sufficient proof of glacial origin, but it is admitted that no boulders have been found showing striation due to ice-action, nor has any glaciated rock-surface been found. Such evidence, however, can hardly be expected, because the boulders are all more or less decomposed owing to the great power of the ground-water in removing silica; and, if the limestone ever presented the features of a glaciated surface, it has been so much modified by solution owing to the action of ground-water since then, that all traces of those features must have disappeared. Large unweathered boulders of corundum are present in some of the beds, but their hardness would make the appearance of ice-scratches improbable.

Unfortunately, the pale and uniform colouring of the bulk of the clays and boulder-clays makes it hard to obtain photographs showing clearly the resemblance to Pleistone glacial deposits. A number of photographs is submitted, however, that will, it is hoped, do something towards this. The petrology of the Gopeng Beds is described in detail. The most interesting point revealed is that the ice from which the detritus was derived passed over a stanniferous granite-mass, and in consequence the Gopeng Beds carry tin-ore throughout, though sometimes in very small quantities. This tin-ore is an original constituent of the beds, but they have been further enriched by tin-ore derived from the Mesozoic granite at their junction with the granite and in the neighbourhood of veins from the granite that have risen through the limestone.

The faulting in the Gopeng neighbourhood, the general structure of the country, and the age and origin of the Gopeng Beds are discussed in detail. The Gopeng Beds are considered to be the equivalent in time of the Talchir boulder-beds of Orissa; but a petrological similarity is wanting, because the Gopeng Beds were derived from a mass of stanniferous granite the position of wnich is at present unknown.

November 22nd, 1911.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

The following communications were read:—

1. 'Petrological Notes on Guernsey, Herm, Sark, and Alderney. By Prof. T. G. Bonney, Sc.D., LL.D., F.R.S., F.G.S., and the Rev. Edwin Hill, M.A., F.G.S.

The authors returned to these islands, after an interval of nineteen years, in order to give futher study to the relations of the igneous masses and especially of certain dyke-rocks. As they had themselves suspected in 1891, and as Mr. J. Parkinson had announced in 1907, the old distinction between diorite and syenite could not be maintained; but there existed, especially in Guernsey and Alderney, a dioritic magma, which underwent differentiation. The results of this are described, the most basic being found at Fort Albert (Alderney), and Bon Repos Bay (Guernsey), and the most acid, which are really tonalites, more especially in the north-west of the latter island. These and a felspathic variety sometimes intrude, sometimes pass into the others, so they also must have been at high temperature. The so-called 'granites' at the two ends of Sark are hornblendic, the southern one being really a tonalite; so are those of Alderney, Herm, Jethou, and Guernsey, and it is suggested that these granites may be yet more acid terms in a differentiation series.

Of the numerous dykes the most acid are either aplitic micro-granites or quartz-felsites; the latter being the rarer and probably later in date. Some of the former at Castle Cornet exhibit an interesting structure. Here diorite cuts gneiss, and has partly melted down a little of it. Microgranite has also cut and melted some of the diorite, the result being a streaked red-and-green rock. Diabase-dykes are common, and mica-traps have been found in all the islands except Herm. The former almost invariably cut the microgranitic dykes, but are cut by the quartz-felsites.

At Pleinmont, in the south-west of Guernsey, a mass resembling a greenstone proves, as mentioned by the late Père Noury, to be sedimentary. This has been examined and is considered to be, like the 'argillites' of Jersey, Brioverian in age. It is cut by dykes of quartz-felsite and by one of diabase (older than these).

The time-relations of the several rocks are discussed. The gneiss of Guernsey, a pressure-modified granite, is the oldest, and had acquired its structure before the intrusion of the diorites. They were followed by the hornblendic granites, and these by the aplitic microgranites. All were pre-Cambrian, and perhaps even the last was older than the Brioverian. The date of the diabase-dykes is more uncertain. They are apparently earlier than the quartz-felsite dykes which may possibly be of the same age as the acid lavas below the conglomerate of Eastern Jersey, now regarded as basal Cambrian; but in Alderney two diabase-dykes cut the grès feldspathique. There is, however, reason to think that these dykes are of more than one age. The mica-traps are probably late Palæozoic.

2. 'The Evolution of *Inoceramus* in the Cretaceous Period.' By Henry Woods, M.A., F.G.S., Lecturer in Palæozoology in the University of Cambridge.

December 6th, 1911.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

The following communication was read:—

'The Faulted Inlier of Carboniferous Limestone at Upper Vobster (Somerset).' By Thomas Franklin Sibly, D.Sc., F.G.S.

The three small masses of Carboniferous Limestone at Luckington, Upper Vobster, and Tor Rock, Vobster, respectively, which lie in the overfolded Coal Measures of the southern portion of the East

Somerset Coalfield, have been the subject of comment and speculation by many writers since two of them were first noticed by Buckland & Conybeare.

The Upper Vobster inlier is by far the largest of the three. Intermediate in position, it lies rather less than a mile to the north of the main outcrop of the Carboniferous Limestone of the Eastern Mendips. This inlier has been dissected to a remarkable extent by quarrying operations ; and its structure is described in detail in the present paper.

The northern and eastern portions of the inlier are concealed by a thin covering of Lias, but its maximum width from north to south is probably little, if at all greater than 400 yards : while the proved east-and-west extent of the Carboniferous Limestone is about 1100 yards.

From personal observation, combined with important evidence recorded by previous investigators, the author has arrived at the following general conclusions:—

(1) The inlier is apparently a lenticular mass of Carboniferous Limestone, grits, and shales, superimposed upon the overfolded strata of the Coal Measures by powerful thrust-movements.

(2) It comprises (*a*) a Northern Limestone Mass, and (*b*) a Southern Limestone Mass, separated by (*c*) a Grit-and-Shale Mass.

(3) The beds of the Grit-and-Shale Mass are in faulted relation to the Carboniferous Limestone on both sides. On the northern side, the immediately adjacent beds of limestone represent part of the *Seminula* Zone ; on the southern side, the adjacent beds belong to the Lower *Dibunophyllum* Zone. On both sides the limestones are locally distorted.

(4) In the Northern Limestone Mass, Vobster Quarry exposes over 500 feet of *Seminula* Beds, overfolded towards the north-west, and dipping south-eastwards at an angle of about 135°.

(5) In the Southern Limestone Mass, where portions of the Lower *Dibunophyllum* Zone and the Upper *Seminula* Zone are exposed, the strata are locally overfolded northwards.

(6) The beds of the Grit-and-Shale Mass comprise quartzites which must certainly be assigned to the Millstone Grit. They also include shales, with intercalated fine-grained sandstones, of considerable thickness. Possibly this mass includes the lowest beds of the Coal-Measures, in addition to a portion of the Millstone Grit.

(7) In most of the sections of Carboniferous Limestone, signs of the immense stresses to which the strata have been subjected are very evident. The beds are often distorted, while slickensides and calcite-veins are extensively developed on both a large and a small scale.

The occurrence of a lamellibranch-fauna at the top of the *Seminula* Zone is recorded as a feature of special interest.

XVIII. *Intelligence and Miscellaneous Articles.*

To the Editors of the Philosophical Magazine.

University College, Galway,
June 18, 1912.

GENTLEMEN,—

I AM anxious to correct a statement made in a paper in the May number, p. 751, that the effect of exposing a metal to ultra-violet light is to make it more electro-positive to other metals. As a matter of fact, the contrary is the case: the metal becomes more electro-negative. It is easy to show, for example, that the contact difference of potential between aluminium and copper can be reduced almost to one half of its original amount, by exposing the aluminium to ultra-violet rays. On the other hand, Röntgen rays, at any rate according to some experiments made in the case of zinc, have the effect of making a metal more electro-positive.

Yours faithfully,
ALEXANDER ANDERSON.

THE QUATERNIONIC FORM OF RELATIVITY.

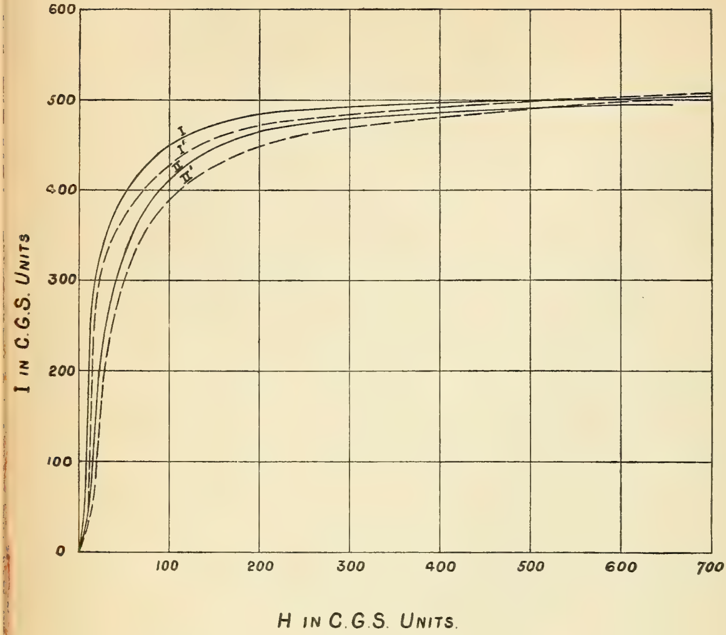
To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE appearance of Prof. Silberstein's paper entitled "The Quaternionic Form of Relativity" in the May issue of the Phil. Mag. is a welcome sign that continental mathematicians, who have already largely availed themselves of various systems of vector notation, are perhaps awakening to the suitability of quaternions in such a connexion. Minkowsky (see footnote p. 79, *Nach. Gött.* 1908) must have had such an idea, but decided in favour of the matrix notation. The quaternion form of the Hertz-Heaviside equations was given by the present writer at the British Association Meeting at Dublin (1908), and had been given by him in lectures for some years previously. An application of quaternions to the Relativity Principle will be found in a paper, vol. xxix. Section A, No. 1, Proc. Irish Academy (read Feb. 1911). Other writers, such as Somerfeld, subsequent to Minkowsky, have used the four-dimensional vector. The obvious defect of this latter method is that it involves a second kind of vector having six components. Beyond this, however, the quaternion has the advantage of being asymmetrical, the time-scalar occupying a different position from the space-vector. It is thus more in touch with real phenomena. For no matter what view we take of relativity, the physical methods of measuring time are quite different from those of measuring spaces, and the flexibility of the quaternion product allows us to put our results at once in a form suitable, if need be, for numerical computation.

Yours truly,
ARTHUR W. CONWAY.

Fig. 3.

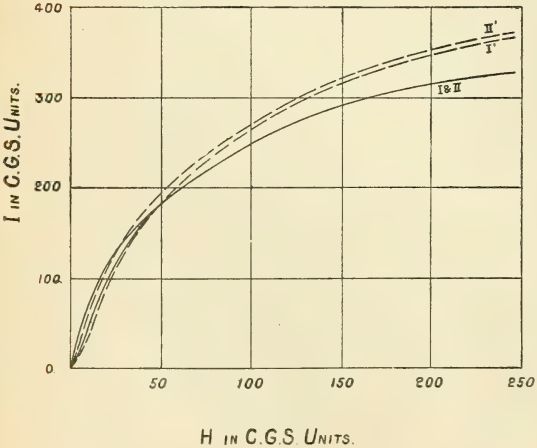


Specimen of Pure Nickel.

I & I', Specimen in Annealed Condition.
II & II', " " Quenched "

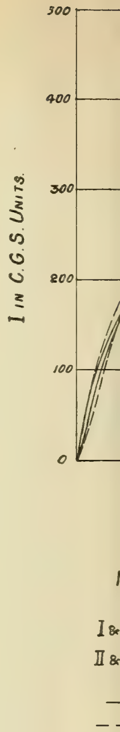
——— Specimen tested at Room Temperature.
- - - - " " " —190°C.

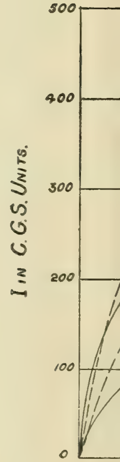
Fig. 4.



Manganese-Nickel Specimen; 5% Mn.

I & I', Specimen in Annealed Condition.
II & II', " " Quenched "





I&I
II&II

Fig. 10.

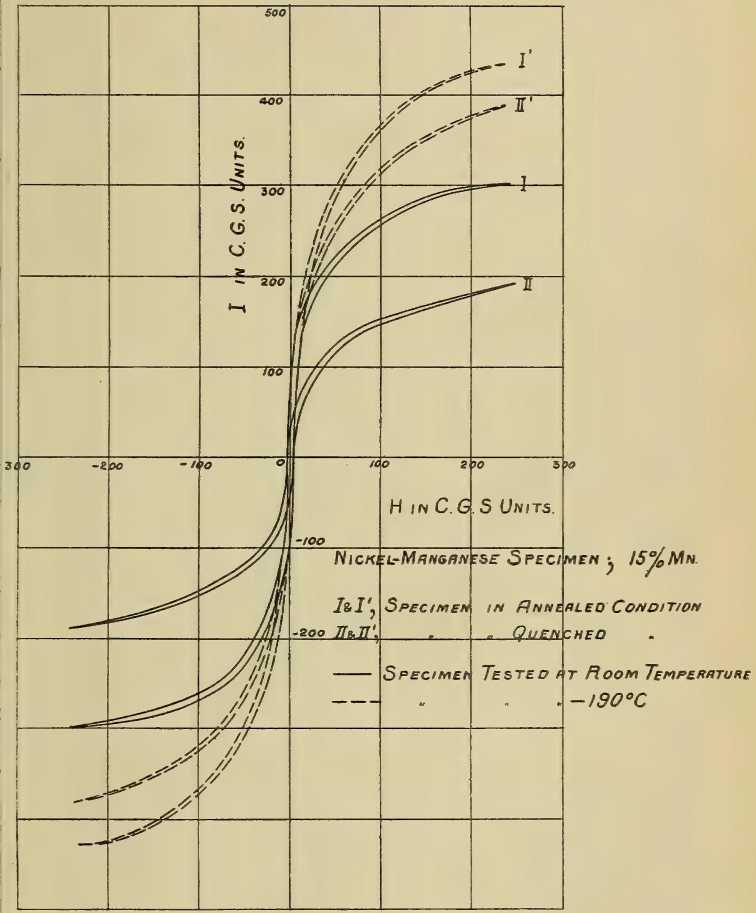
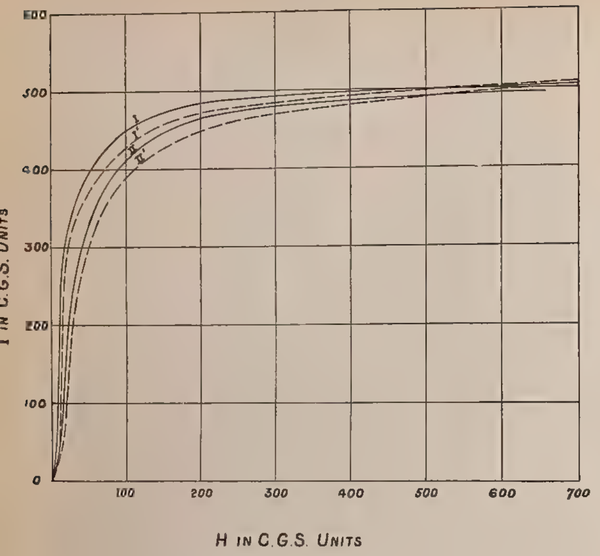

500
400
300
200
100
-100
-200
I in C. G. S. Units.
300
-200
-100
0
100
200
300
H in C. G. S Units.
I'
II'
I
II
Nickel-Manganese Specimen; 15% Mn.
I & I', Specimen in Annealed Condition
II & II', " " Quenched .
—— Specimen Tested at Room Temperature
- - - " " " -190°C

Fig. 3.

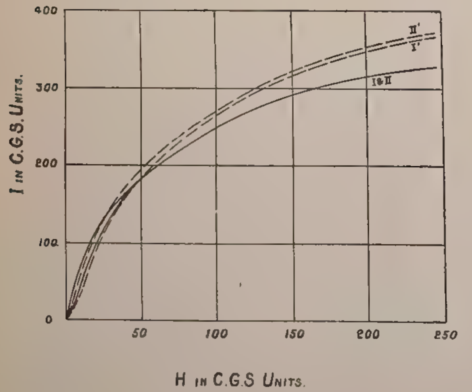


Specimen of Pure Nickel.

I & I′, Specimen in Annealed Condition.
II & II′, " " Quenched "

—— Specimen tested at Room Temperature.
- - - - " " " —190°C.

Fig. 4.

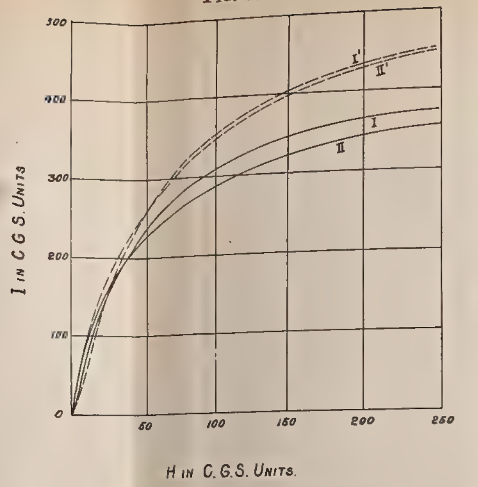


Manganese-Nickel Specimen ; 5% Mn.

I & I′, Specimen in Annealed Condition.
II & II′, " " Quenched "

—— Tested at Room Temperature
- - - - " " —190°C.

Fig. 5.

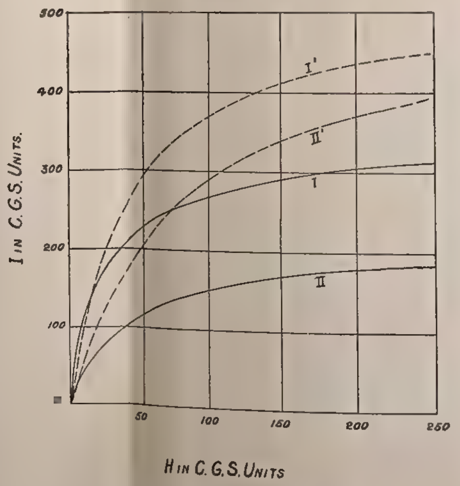


Manganese-Nickel Specimen ; 10% Mn.

I & I′, Specimen in Annealed Condition
II & II′, " " Quenched "

—— Tested at Room Temperature
- - - " " —190° C.

Fig. 6.

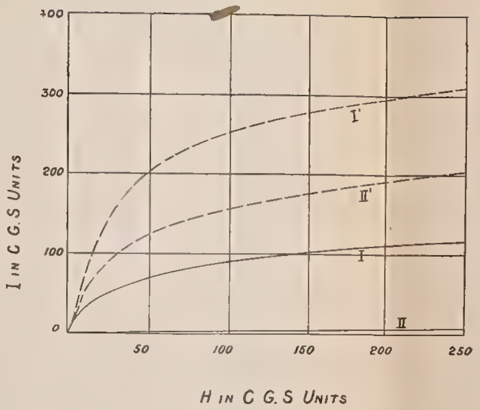


Nickel-Manganese Specimen, 15% Mn.

I & I′, Specimen in Annealed Condition.
II & II′, " " Quenched "

—— Tested at Room Temperature
—190° C

Fig. 7.

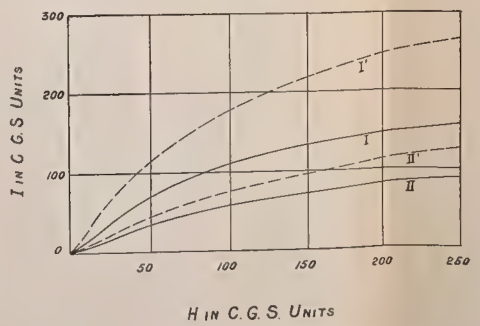


Nickel-Manganese Specimen; 20% Mn

I & I′, Specimen in Annealed Condition
II & II′, " " Quenched "

—— Tested at Room Temperature
- - - " " -190° C

Fig. 8.

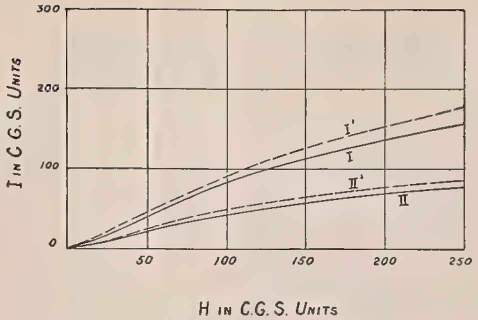


Nickel-Manganese Specimen; 25% Mn.

I & I′, Specimen in Annealed Condition
II & II′, " " Quenched "

—— Tested at Room Temperature
- - - " " -190° C

Fig. 9.

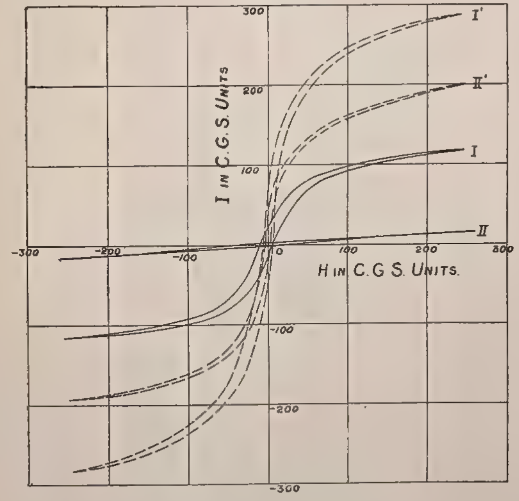


Nickel-Manganese Specimen; 30% Mn

I & I′, Specimen in Annealed Condition
II & II′, " " Quenched "

—— Tested at Room Temperature
- - - " " -190° C.

Fig. 11.

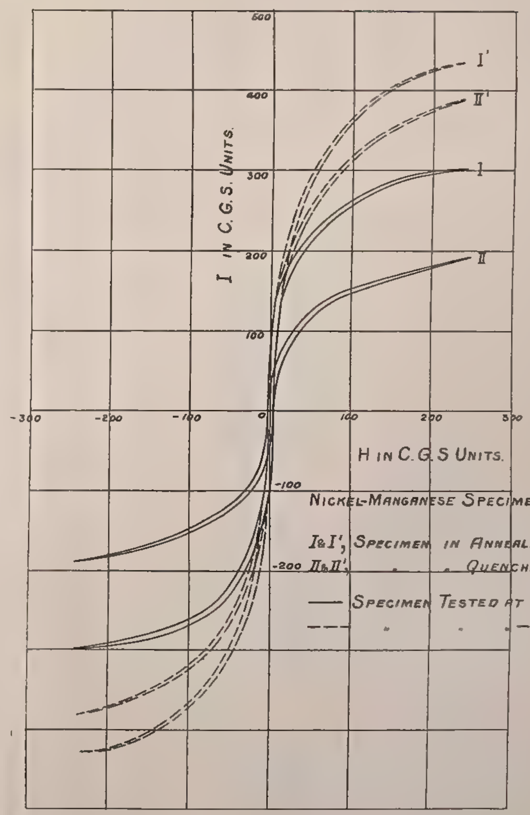


Nickel-Manganese Specimen ; 20% Mn

I & I′, Specimen in Annealed Condition
II & II′, " " Quenched "

—— Specimen Tested at Room Temperature
- - - " " -190°C.

Fig. 10.



Nickel-Manganese Specimen ; 15% Mn.

I & I′, Specimen in Annealed Condition
II & II′, " " Quenched "

—— Specimen Tested at Room Temperature
- - - " " " -190°C

I IN C.G.S. UNITS

linder burst by the ure. The inner hole to $\frac{3}{8}$ in.

Fig. 9.

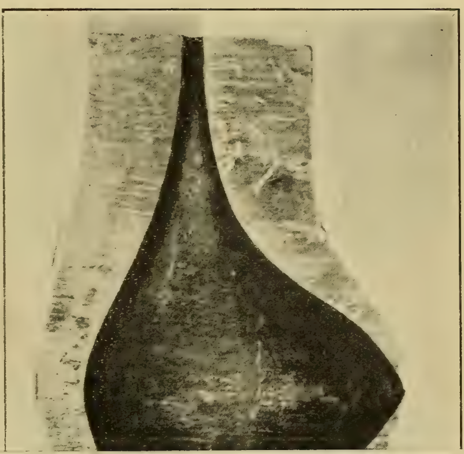
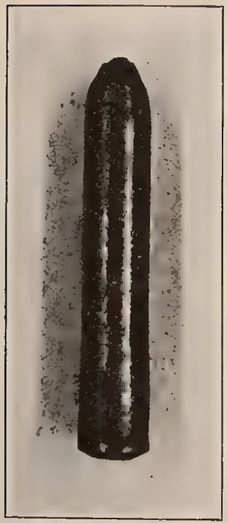
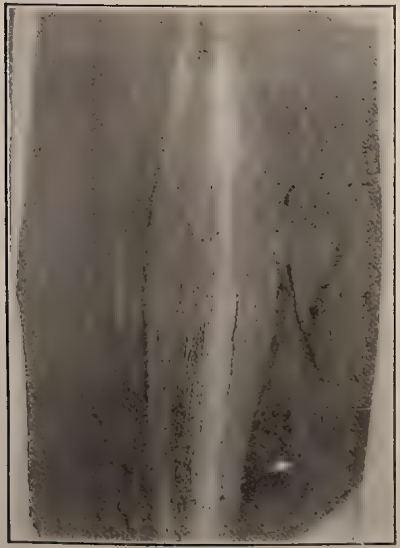


FIG. 2.



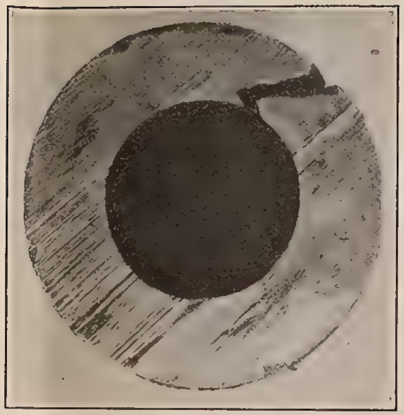
Photograph of a "pinched-off" specimen, ruptured in the apparatus of Fig. 1.

FIG. 4.



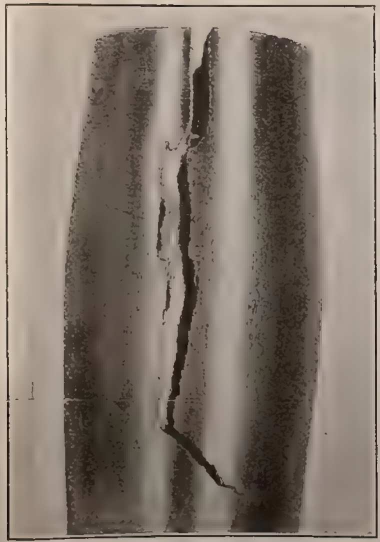
One of the halves of a cylinder of Bessemer steel (originally 4 in. in external diameter) ruptured by the application of internal pressure. The inner hole has stretched from ½ in. to 1⅜ in.

FIG. 5.



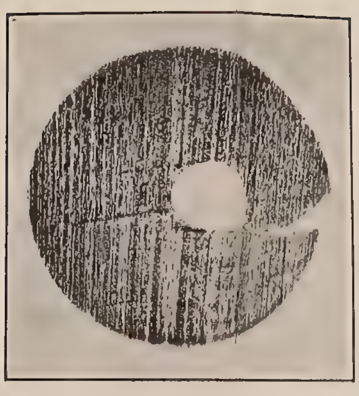
Cross section of a cylinder of Bessemer steel ruptured by the application of internal pressure. This cylinder was originally 2 in. outside and ½ in. inside diameter. The inner hole has been stretched to 1⅜ in.

FIG. 6.



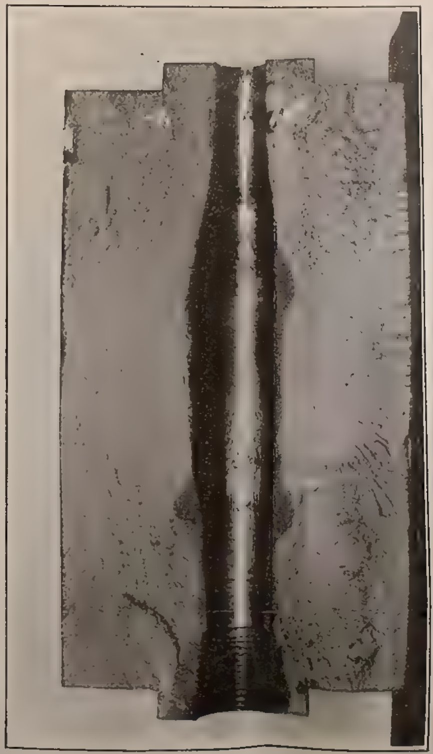
View of the outside of the cylinder of Fig. 5 taken before the section was made.

FIG. 7.



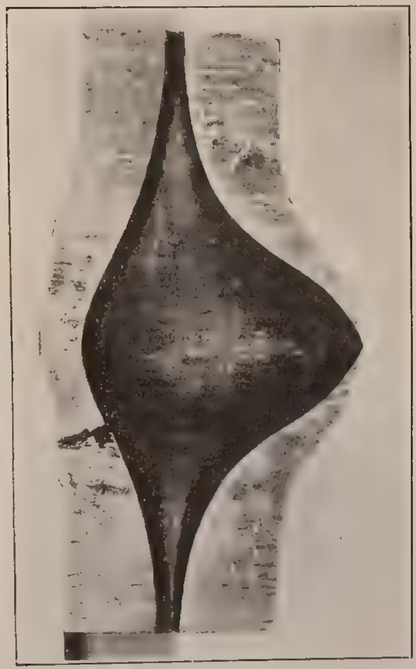
Cross section of a copper cylinder burst by the application of internal pressure. The inner hole has been stretched from ⅛ in. to ⅜ in.

FIG. 8.

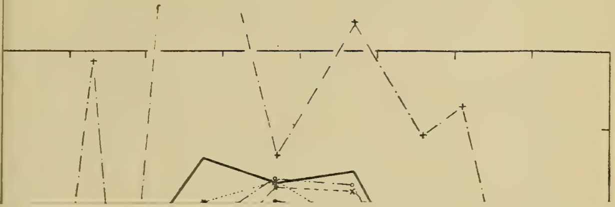


One of the halves of a cylinder of tool steel split by the application of internal pressure. The inner hole has stretched from ½ in. to 1⅛ in. The maximum pressure withstood by this cylinder was 30,000 atmos.

FIG. 9.



Longitudinal section of a cylinder of lead burst by the application of internal pressure. The elongation at the outside at the locality of rupture is over 300 per cent.



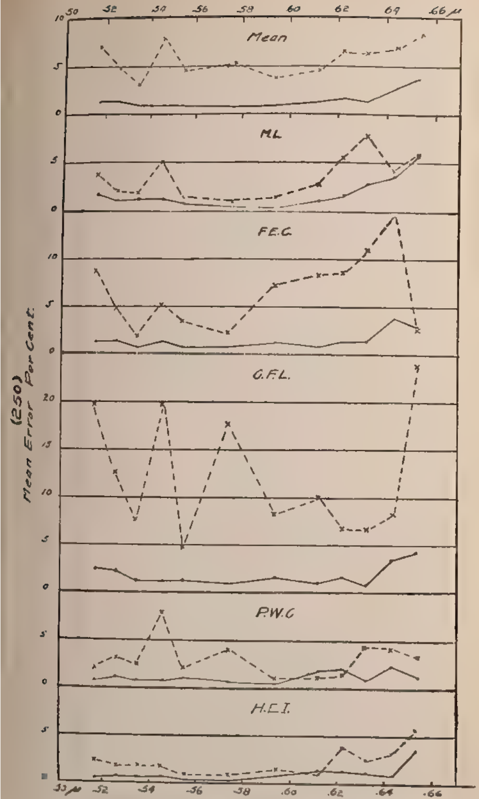


Fig. 2.—Sensibility of Flicker and Equality of Brightness Methods. (High Illumination.)

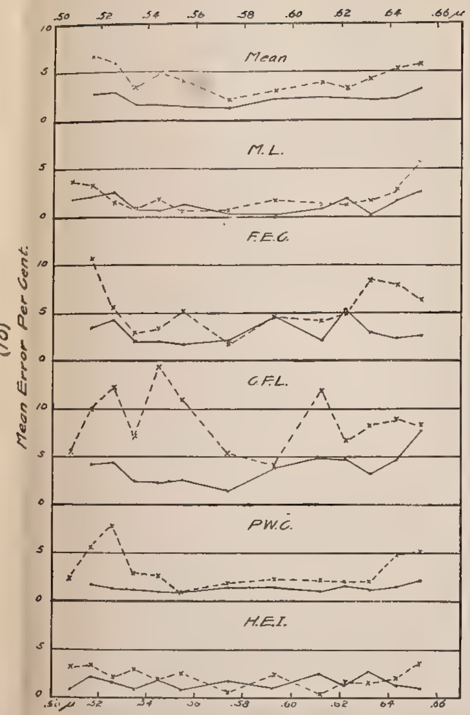


Fig. 3.—Sensibility of Flicker and Equality of Brightness Methods. (Low Illumination.)

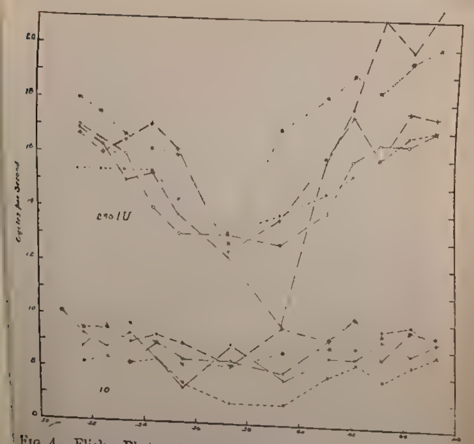


Fig. 4.—Flicker Photometer Speeds. (High and Low Illuminations.)

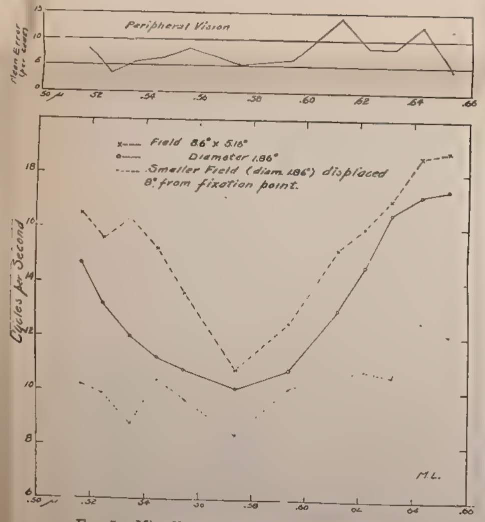


Fig. 5.—Miscellaneous Speed and Sensibility data.

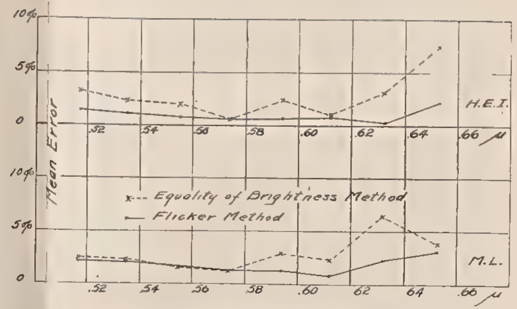


Fig. 6.—Reproducibility of Measurements. (Mean of 5 observations taken over a period of Two Months.)

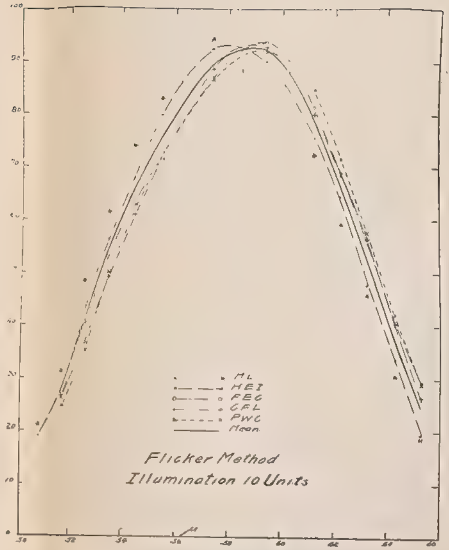


Fig. 7.—Luminosity Curves of Five Observers.

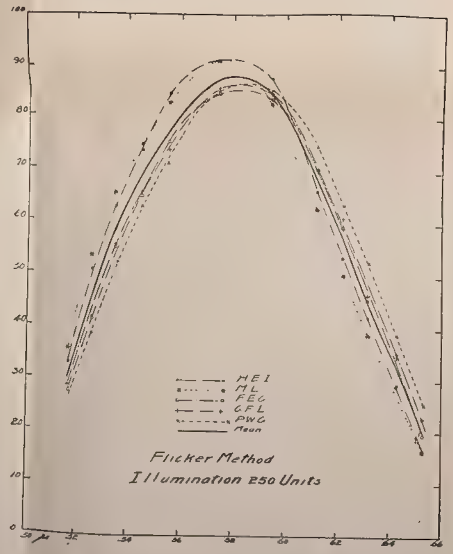


Fig. 8.—Luminosity Curves of Five Observers.

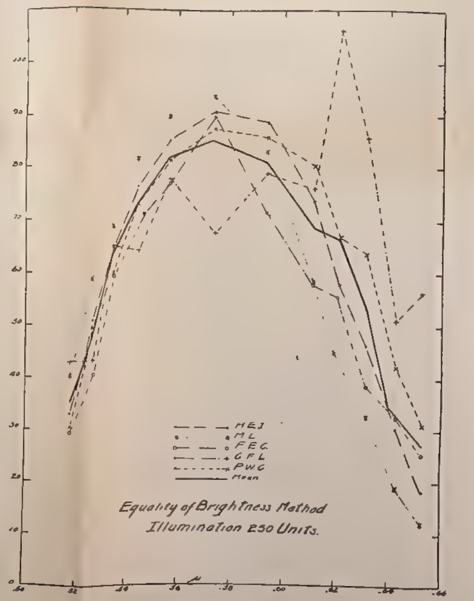


Fig. 9.—Luminosity Curves of Five Observers.

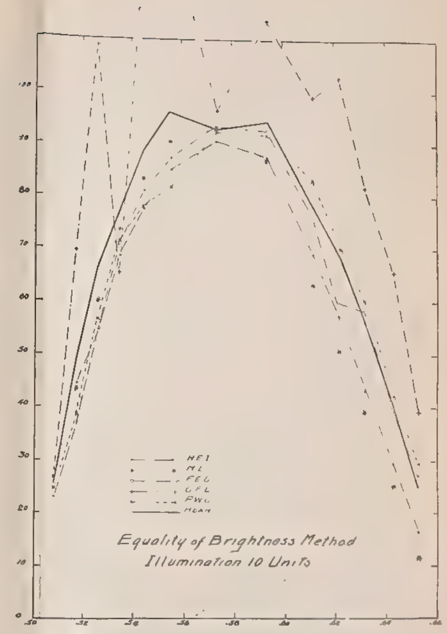


Fig. 10.—Luminosity Curves of Five Observers.

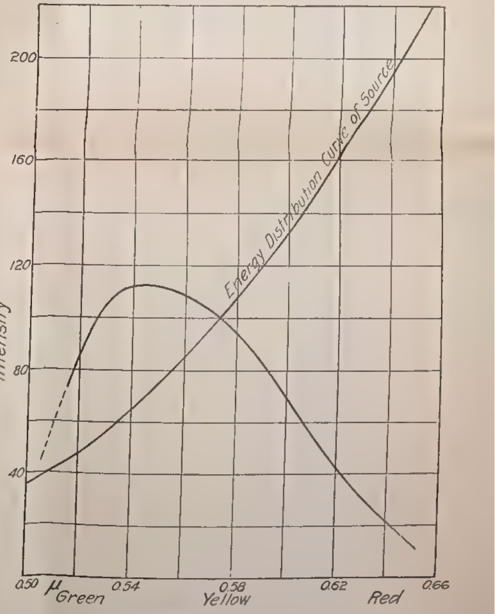


Fig. 11.—Mean Luminosity Curve for Normal Spectrum.

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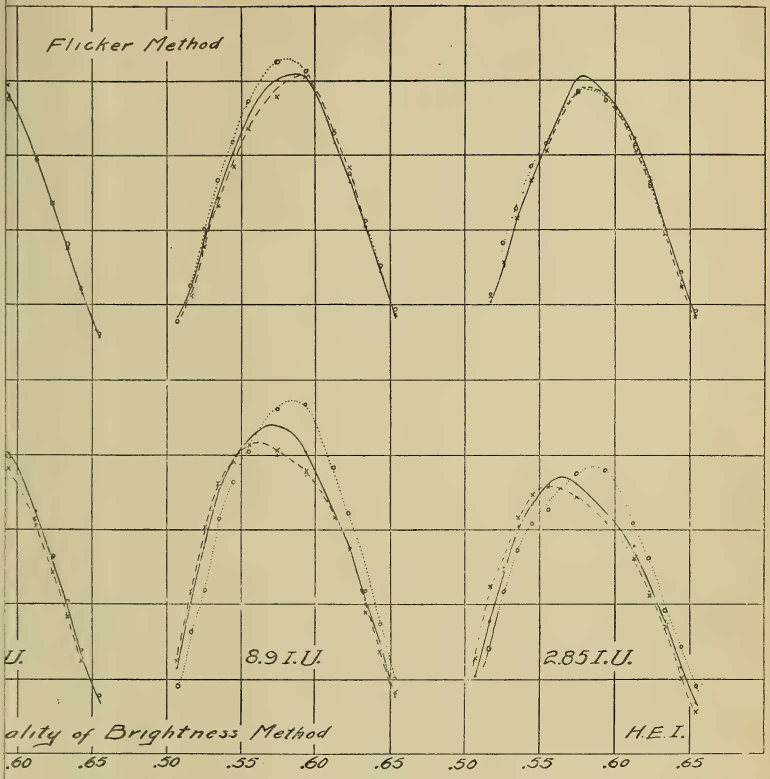


I —Effect of Changing Size of Field

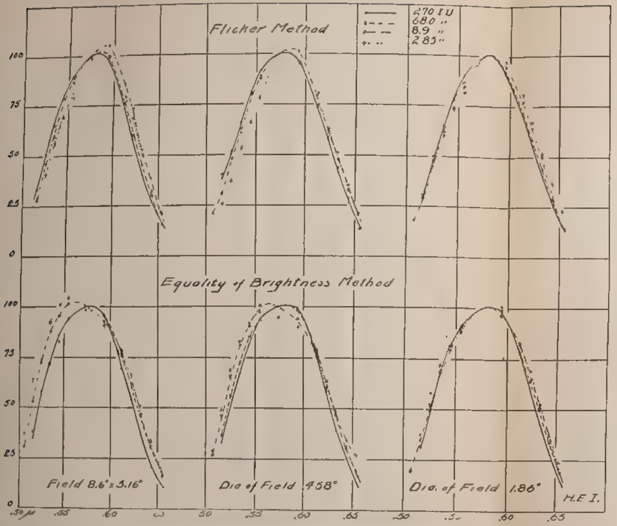


Plate I.—Effect of Changing the Illumination.

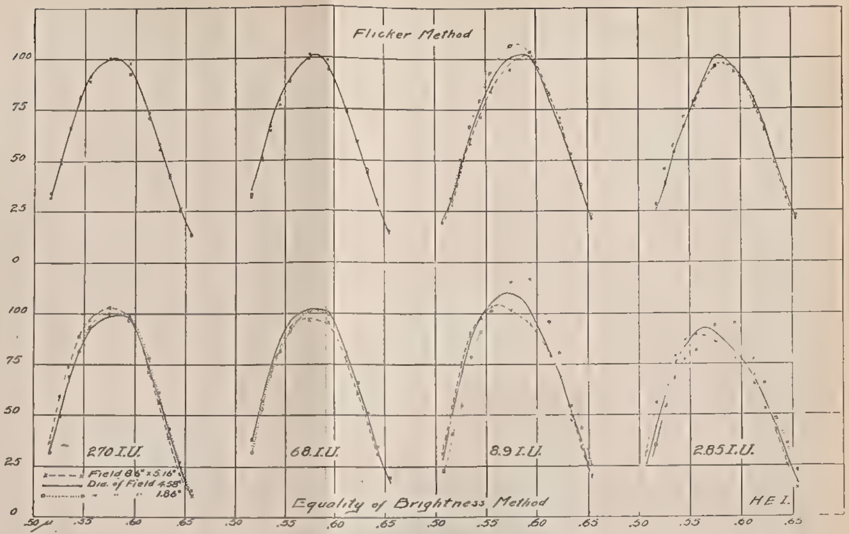


Plate II.—Effect of Changing Size of Field.

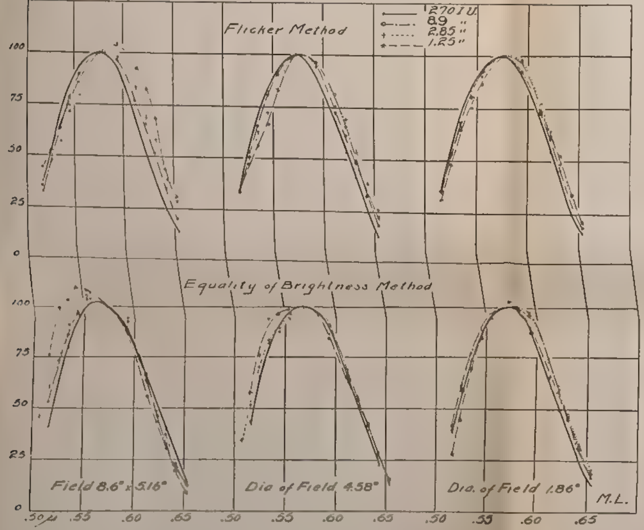


Plate I a.—Effect of Changing the Illumination.

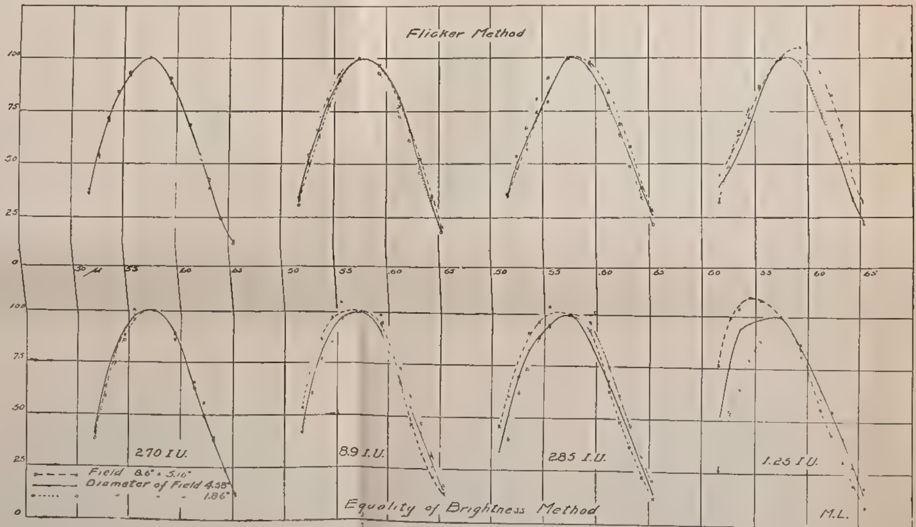


Plate II a.—Effect of Changing Size of Field.

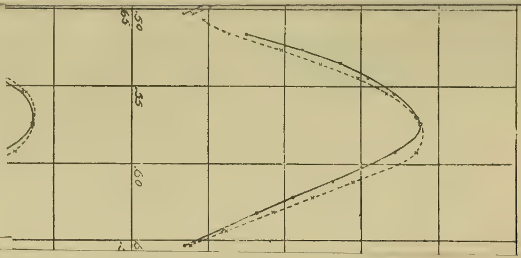


FIG. 2.

FIG. 3.

VI.

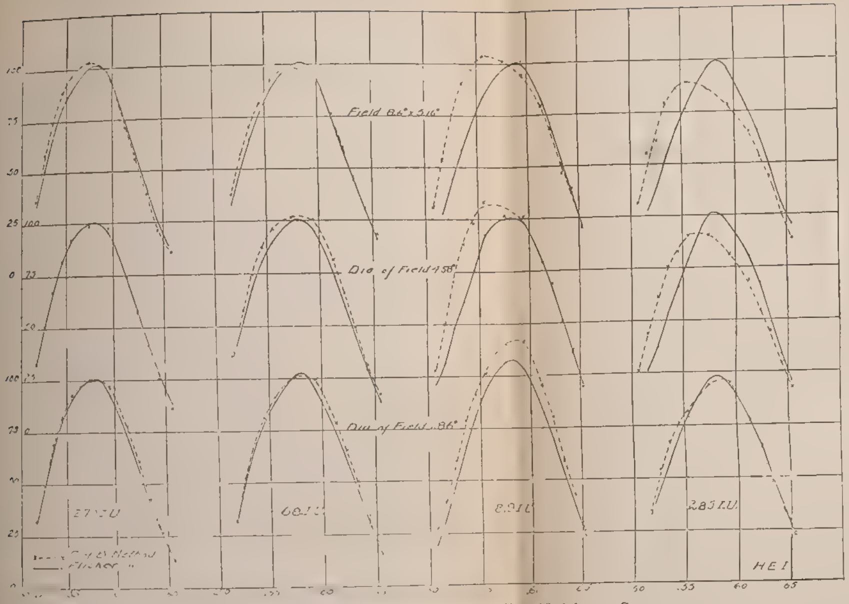


Plate III.—Relative Position of Flicker and Equality of Brightness Curves.

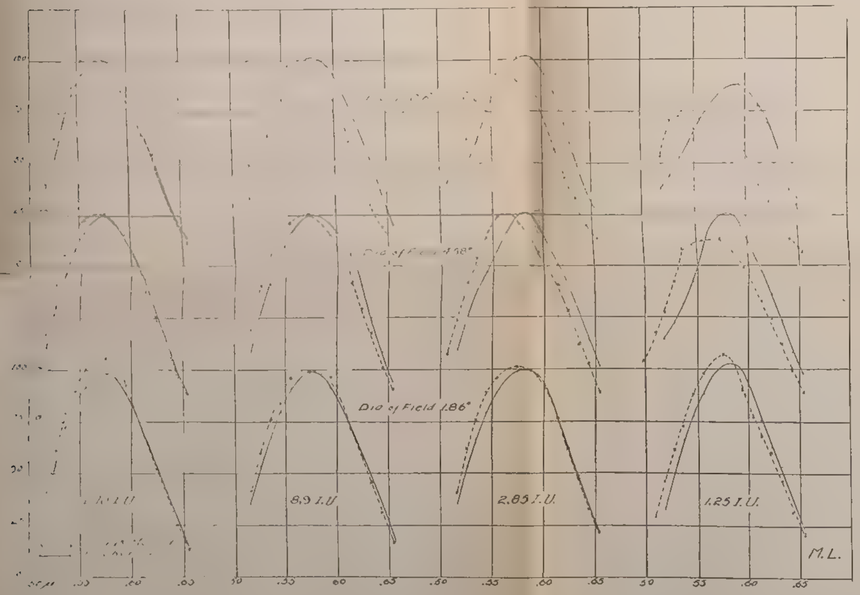


Plate III *a*.—Relative Position of Flicker and Equality of Brightness Curves.

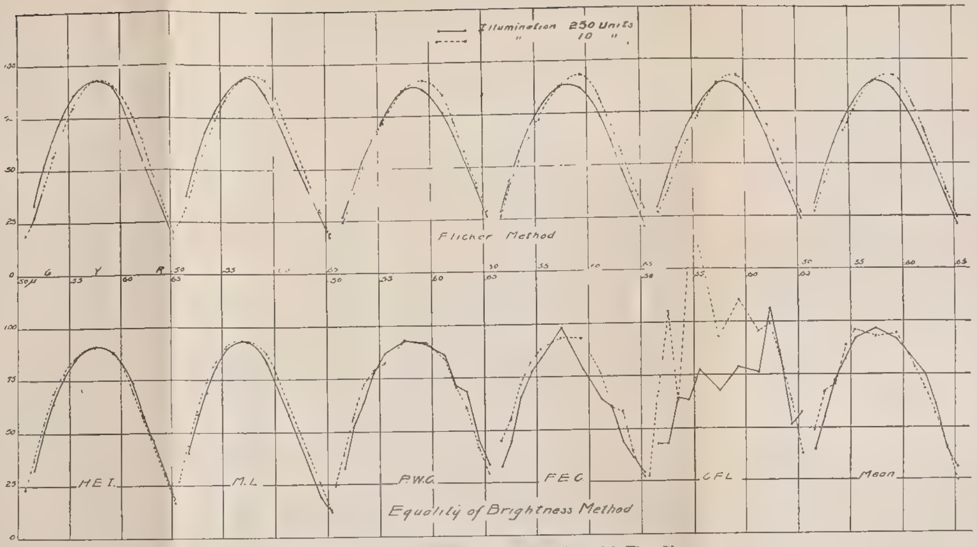


Plate IV.—Effect of Changing the Illumination with Five Observers.

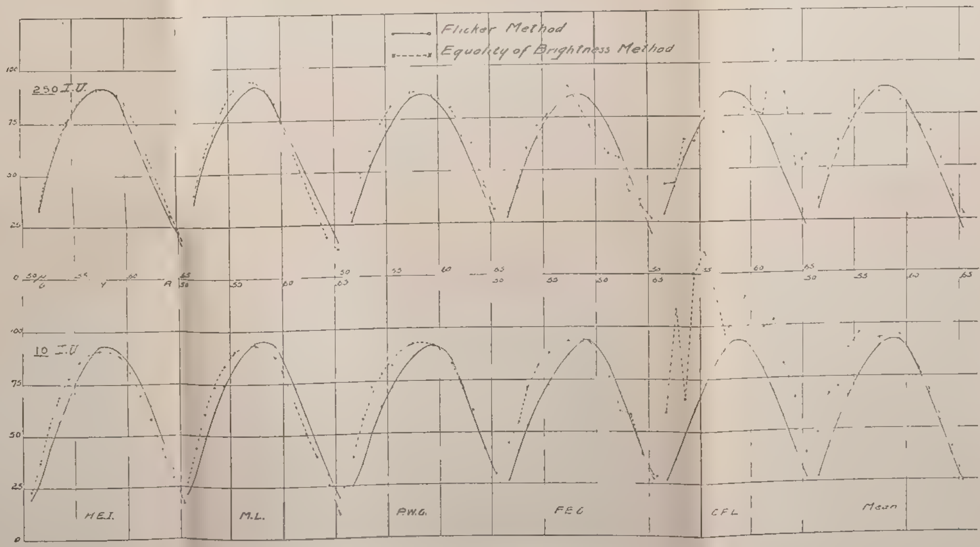
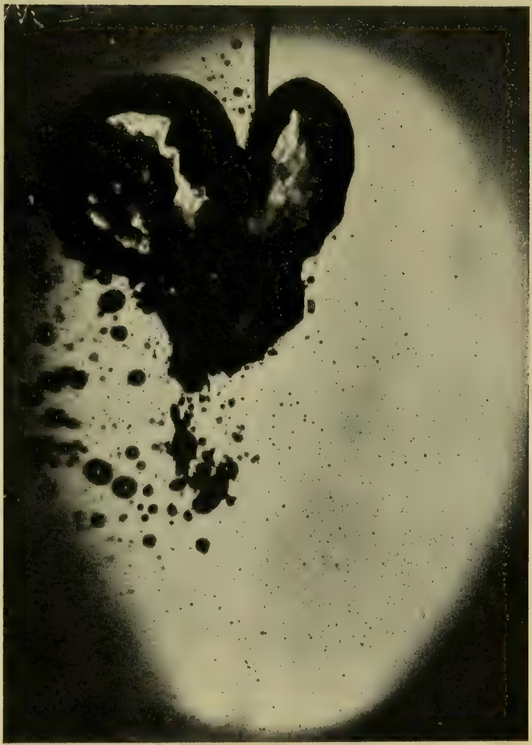


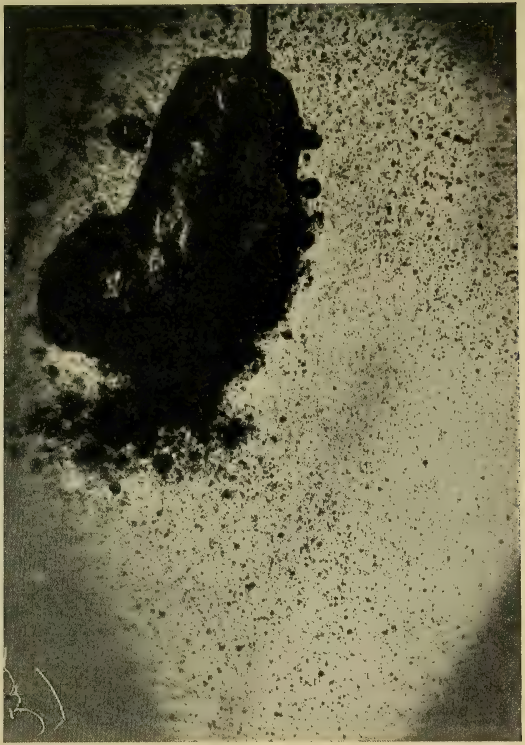
Plate V.—Relative Positions of the Two Kinds of Curves for the Five Observers.

Photographs of a bubble of CO_2 being formed in:—



Water.

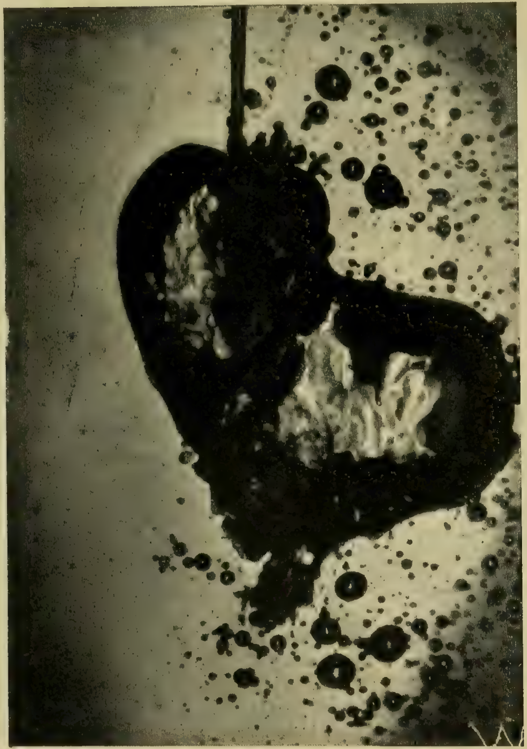
Fig. 2.



$0{\cdot}1\,^{\circ}/_{\circ}$ *aqueous solution of acetic acid.*

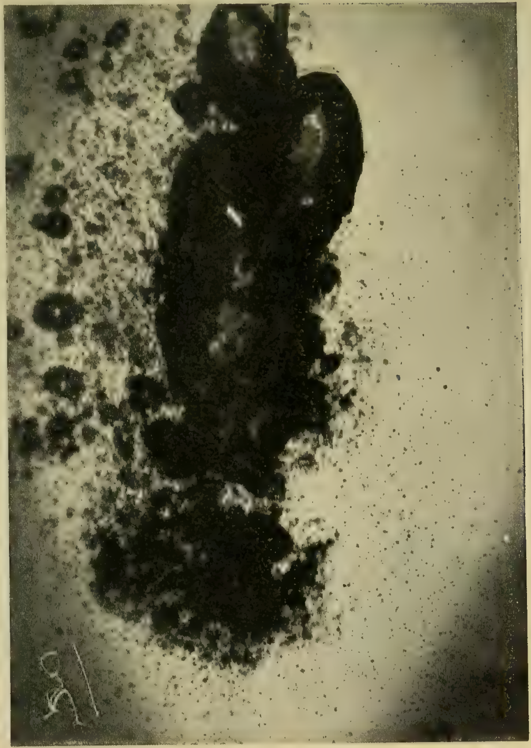
Fig. 3.

Photographs of a bubble of CO_2 being formed in:—



Water.

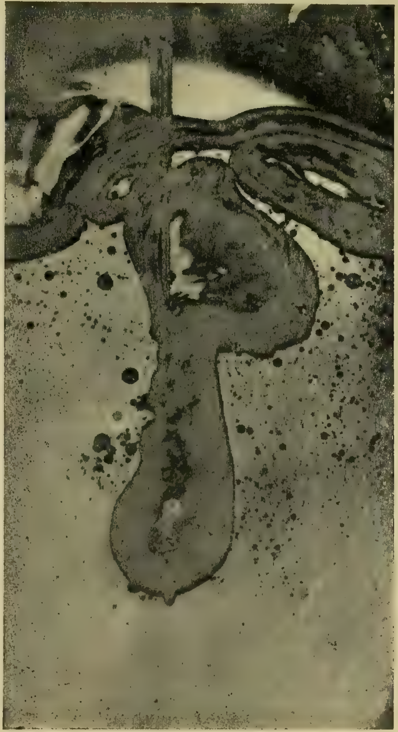
FIG. 4.



$0{\cdot}1^{\circ}/_{\circ}$ *aqueous solution of acetic acid.*

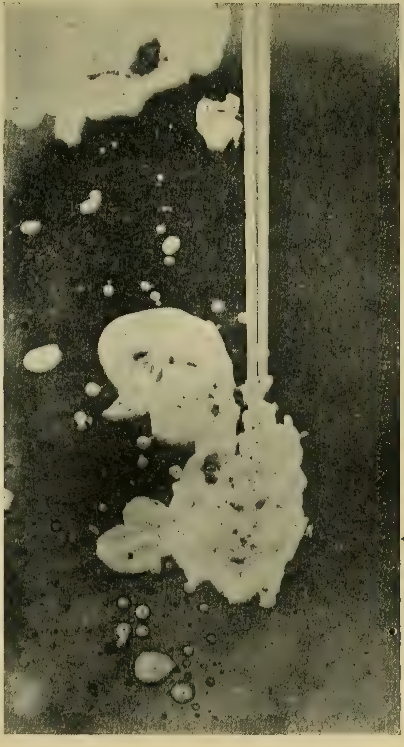
FIG. 5.

Photographs of a bubble of CO_2 being formed in:—



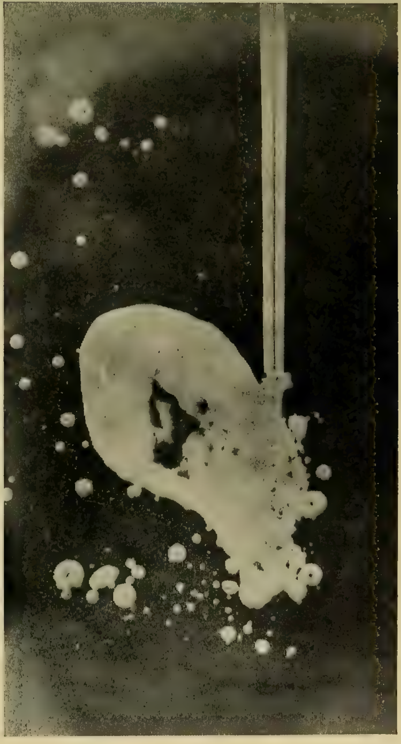
0·1°/。 aqueous solution of acetic acid.

FIG. 6.



Water.

FIG. 7.



0·1°/。 aqueous solution of sulphuric acid.

FIG. 8.

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[SIXTH SERIES.]

AUGUST 1912.

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XIX. *Further Experiments on Positive Rays.* *By* Sir J. J. Thomson, *O.M.*, *F.R.S.*[*]

[Plate IX.]

THE experience gained in the course of the investigations of these rays has led to some modifications in the apparatus which increase the brightness of the positive rays and thereby facilitate their investigation. The following are the most important changes made since the publication of my paper "On a New Method of Chemical Analysis," Proc. Roy. Inst. 1911.

Shape of the front of the Cathode and its position in the Tube.—Cathodes of various shapes have been tried—flat, concave, and convex; the best results have been obtained with a cathode shaped so that its section has the form represented by C in fig. 1 (p. 210).

The tubes we use for the discharge are spherical flasks about 30 cm. in diameter, the cathode being in the neck of the flask. The brightness of the rays is very much affected by the extent to which the cathode projects into the flask; if the cathode either extends far into the flask or is far back in the neck, the rays are comparatively feeble: the best position is when the front of the cathode comes nearly flush with the opening into the flask. The space between the sides of the cathode and the neck of the flask must be small, otherwise when monatomic gases such as helium or argon are used there is a considerable deposition of metal on the neck of the flask ; the discharge then tends to start from this deposit instead of from the cathode, and very few positive rays pass down through the hole in the cathode.

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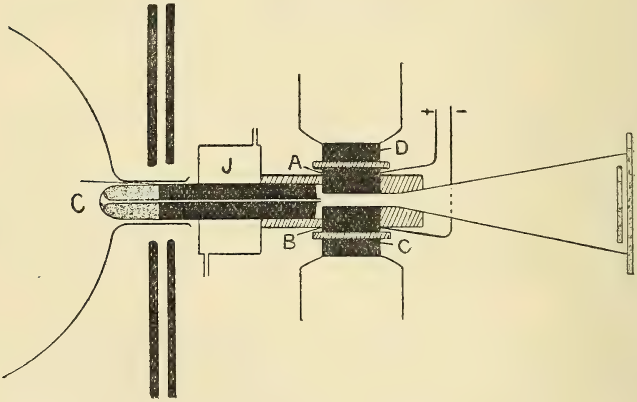
[*] Communicated by the Author.

For the channel through the cathode we generally use fine copper tubes drawn out until the opening is sufficiently reduced ; the length of the tube is about 8 cm., and the diameters of the tubes we have used vary from ·1 to ·01 mm.

It is a matter of some difficulty to get the finest tubes sufficiently straight to allow a particle moving in a straight line to pass through the tube without striking against the sides. The following method was used when it was necessary to reduce the size of the tube as much as possible. Two flat pieces of steel were made as accurately plane as possible by the use of surface plates ; a shallow fine scratch was ruled on one of the plates, and the two plates were then bolted together, the scratch making an exceedingly fine channel between the plates. With these very fine tubes it is necessary when taking photographs to give a very long exposure, 2 or 3 hours ; and to adopt special arrangements for keeping the magnetic and electric forces constant during this interval, as fluctuations in the intensity of these forces broaden the lines and neutralize the benefit derived from the smallness of the tube.

Fig. 1.



The photographic plates with which we have obtained the best results are the Imperial Sovereign. Inasmuch as the rays do not penetrate right through the film, the most suitable plates for these experiments might be expected to be those which had very thin films containing as much of the silver salts as possible. Guided by this consideration, I tried the old Daguerrotype silver plates treated with iodine, but did not obtain such good results as with the Sovereign plates.

For some experiments it is important that the magnetic and electric fields used to deflect the rays should be as coterminous as possible, and so arranged that if necessary the length of these fields can be reduced to a few millimetres and the intensity increased sufficiently to give measurable deflexions. The arrangement represented in fig. 1, which was designed by Mr. Aston, has been found to give good results. The soft iron pole-pieces, which have flat plane ends A and B, are in an ebonite box which forms part of the observation-tube, the ends of the electromagnet CD fitting into recesses cut in the outside of the box. The flat ends of the pole-pieces, which are insulated, are used as the plates to produce the electric field. Care must be taken that the positive rays do not strike either ebonite or glass, as if they do they charge up the surface and produce an electric field which deflects the rays. Earth-connected pieces of tinfoil were placed on these insulators to prevent any charge of electricity accumulating upon them. A water-jacket J is placed round the observation-tube to prevent the wax getting hot and giving off vapour.

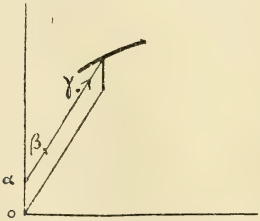
We shall now proceed to discuss some results obtained with this apparatus.

Secondary Lines on the Photographs of the Positive Rays.—These photographs show lines of two types: one type consists of a series of arcs of parabolas which, when the deflexion due to the electrostatic field is horizontal, start in most cases from points lying on a straight vertical line. Since the horizontal electrostatic deflexion is inversely proportional to the kinetic energy of the charged particles, this shows that the maximum kinetic energy possessed by the particles producing these lines is the same for each kind of particle.

These parabolic arcs are often of considerable length, indicating that there is a considerable range of velocities among the particles of the same kind. The ratios of the *latera recta* of the different parabolas are equal to the ratios of the values of e/m for the particles producing the parabolas, and are independent of the strength and distribution of the electric or magnetic fields. We attribute the formation of these parabolic arcs to particles which were charged before they entered the electric and magnetic fields, and which have retained their charges unaltered during their passage from one end of the field to the other. The value of e/m for the particle producing a line of this type can be determined at once by comparing the *latus rectum* of its parabola with that of a parabola due to a known particle, say the atom of hydrogen, or the mercury atom ; if the intensities of the electric and magnetic fields are known, we can determine the absolute value of e/m for any parabola without using any comparison lines. We shall call the lines of this type the primary lines.

When, however, the pressure of the gas traversed by the rays after passing through the cathode is not too low, there are other lines to be seen on the plate which have quite different properties from the primary lines (Pl. IX. fig. 2). They form curves of fairly uniform intensity which do not stop short at a finite distance from the vertical axis but are continued until they meet this axis : in some cases they pass through the origin itself, in others they start from points vertically above or below it. They are to be found on the side of the plate corresponding to negative charges as well as on that corresponding to positive. Their shape and also their position with respect to the primary lines depends upon the disposition as well as on the intensity of the electric and magnetic fields. If care is taken to make the electric and magnetic fields uniform and coterminous, the curves we are discussing become straight lines passing either through the origin or very near to it; examples of these are shown in figs. 3 and 11 (Pl. IX.). We see from the figure that though all the lines of this type pass nearly through the origin, one set actually passes through it, while another starts from a point on the vertical axis a little above it, the curves having the shape shown diagrammatically in fig. 4 *a*. Fig. 4 *b* (Pl. IX.) is a photograph. A careful examination of the plate shows that the lower curve turns up abruptly towards its termination A

Fig. 4 *a*.



and joins the upper one. There are sometimes several pairs of these lines on a plate running up into the primary parabolas due to particles having small atomic weights. The lines due to the heavier particles are often connected with lines corresponding to the lower curve in fig. 4 *a*, while for these heavy particles the upper curve is absent.

The separation of the lines in a pair such as is represented in fig. 4 *a* is much more pronounced when the magnetic field considerably overlaps the electric, and both are fairly uniform. Such a case is represented in fig. 5 (Pl. IX.), which is a reproduction of a photograph taken when the pressure in the observation-tube, *i. e.* the part of the tube between the cathode and the camera, was considerable. It will be noticed that these pairs occur on both sides of the vertical line through the origin, showing that this type of line is produced by negatively as well as by positively charged particles. An interesting point is well brought out by this plate: it will be noticed that there is no fogging of the plate between the two lines, while there is very considerable fogging of the plate below the lower line. In this case there is very little fogging above the upper line, but on other plates the part of the plate above the upper line is also fogged to some extent, though not so much as the part below the lower line; the space between the lines is in all cases free from fogging.

The straightness of the lines when the electric and magnetic fields are uniform shows that the rays which produce any one line must be moving with nearly the same velocity, the fineness of the lines showing that the variations in the velocity must be exceedingly small.

Origin of the Lines.—The lines of the type of the upper one in fig. 4 *a* are due, I think, to particles which passed out from the delivery-tube through the cathode uncharged, but which subsequently, by striking against a corpuscle, lost a corpuscle and became positively charged before they passed out of the reach of the electric and magnetic fields. The lower lines in fig. 4 *a* are due, I think, to particles which were charged when they passed through the delivery-tube in the cathode into the electric and magnetic fields, but which, by combining with a corpuscle, got neutralized before they escaped from these fields; the different points on the curve being due to particles which have gained or lost their charge at different points of their path. Let us consider the first type of secondary, and suppose that, as was the case in most of the experiments, the magnetic field slightly overlapped the electrostatic. In the curve fig. 4 *a* the initial vertical portion $O\alpha$ is due to the particles which acquired their charge after they had left the electric field, but before they had quite passed through the magnetic field, their vertical deflexion being due to the part of the magnetic field which stretches beyond the electric. The portions $\alpha\beta$ near α are due to particles which got their electric charge shortly before they left the electric field, while the portions $\beta\gamma$ further away from α are produced by particles which got charged at an earlier stage in their career.

Let us now consider the effect on the shape of the lines of a want of uniformity in the electric or magnetic fields. Since the lines are straight when the fields are uniform, the different particles which produce a line must all be moving with approximately the same velocity. Let this velocity be v, then if the particle acquired its charge at a distance ξ from the photographic plate, y the vertical displacement at the plate due to the magnetic field is given by the equation

$$y=\frac{e}{mv}\int_0^\xi x\mathrm{H}dx,$$

where H is the magnetic force at a distance x from the plate.

Thus
$$\frac{dy}{d\xi}=\frac{e}{mv}\xi\mathrm{H}_\xi,$$

where H_ξ is the value of H at ξ.

Similarly, if z is the horizontal displacement due to the electrostatic force,

$$z=\frac{e}{mv^2}\int_0^\xi x\mathrm{X}\,.\,dx,$$

where X is the value of the electrostatic force at a distance x from the photographic plate.

We have, therefore,

$$\frac{dz}{d\xi}=\frac{e}{mv^2}\xi\mathrm{X}_\xi,$$

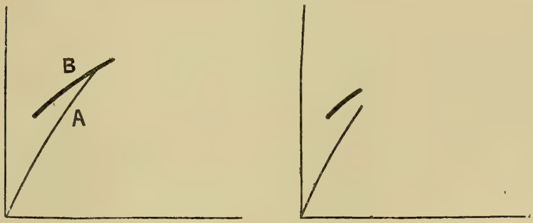
and so

$$\frac{dy}{dz}=v\frac{\mathrm{H}_\xi}{\mathrm{X}_\xi}.$$

And thus the tangent of the angle which the tangent to the curve makes with the horizontal represents the variations in the ratio of the magnetic to the electric forces. Take, for example, the case when the magnetic force extends beyond the plates used to produce the electric field and when the magnetic force gets weaker as we approach the cathode. The curve will start from the vertical line at some distance above the origin, and the curve will get flatter and flatter as we travel upwards from P ; in this respect it will resemble a parabola. This secondary curve must ultimately cut the primary curve corresponding to its particle at a point on the primary produced by a particle moving with the velocity v.

Considerable variations in the shape of the secondary curves may be produced by variations in the distribution of the electric and magnetic fields. Thus, suppose that the delivery-tube for the positive rays extends up to one end of the plates so that at this end there is no place where a charged particle is acted on by magnetic and not by electric forces. Then, if the electric and magnetic fields were coterminous at the other end, the shape of the secondary might be somewhat like that shown in fig. 6, the thick line representing the primary curve.

Fig. 6.

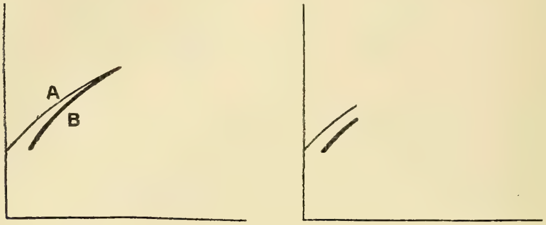


If, however, the magnetic field at the end next the camera overlapped to a considerable extent the electric field, then the secondary curve might resemble that shown in fig. 7, the secondary curve being now above the primary instead of below it as in fig. 6.

Thus, if the secondary curves were not completed on the plate, but stopped, for example, at AB (figs. 6 and 7), we might easily mistake the secondary line for a primary due to a particle which in fig. 7 had a value of e/m greater and in fig. 6 less than the primary to which it really corresponds. This is a point which requires careful attention when we use the curves produced by the positive rays to analyse the gases in the tube.

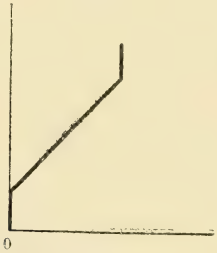
The two photographs reproduced in figs. 8 and 9 (Pl. IX.) show cases in which, by changing the disposition of the magnetic field, the secondary due to the hydrogen atom has been displaced from below its primary to above it.

Fig. 7.



If the delivery-tube for the positive rays did not reach up to the beginning of the plates used to produce the electrostatic deflexion, and the magnetic field overlapped the electrostatic at both ends, dy/dx would be infinite at the beginning and end of the curve, and the secondary curve would be shaped like the one shown in fig. 10.

Fig. 10.



An example of this is shown in the photograph reproduced in fig. 9 (Pl. IX.).

We see from these considerations that a secondary line may suffer considerable variation in position, and there is some danger, unless precautions are taken, that a secondary which has been displaced owing to some change in the distribution of the magnetic or electric fields, might be regarded as a line due to a different kind of particle. When the photographs of the positive rays are used to analyse the gases in the discharge-tube, the lines due to the primary rays are the only ones that can be relied on. The tests for these primary lines are (1) that they must be parabolic, and (2) that there should be a rapid increase in intensity in all these lines at places all situated on a vertical line (if the electrostatic deflexion is horizontal). The first condition is theoretically sufficient except with very special distributions of the electric and magnetic forces; but I have found that in practice the secondaries are not infrequently very approximately parabolic when they are near to their primaries, so that unless a very high degree of accuracy were obtained in the measurement of these lines, their secondary nature might easily escape detection if this were the only test applied.

The secondaries we are now considering arise from the collision of neutral particles with corpuscles; they cannot be produced by collision of the particles with other particles having a mass comparable with that of the neutral particles, for such a collision would deflect the path of the particles, and the lines in the photographs would become much more diffuse than is actually the case. The collisions which ionize the particles are between moving particles and corpuscles which are approximately at rest; the effects of the collision will, however, only depend on the relative motion of the particle and corpuscle, and will be the same as if the particle were at rest and the corpuscle moving with the velocity of the particle. Now in order that a moving corpuscle may ionize an atom or molecule against which it strikes, the velocity of the corpuscle must exceed a definite limit which probably depends to some extent on the nature of the atom or molecule. Let us call this limit for a particular kind of atom V; then in order that an uncharged atom of this kind should be ionized when it strikes a corpuscle at rest, it must move with a velocity greater than V: hence all the secondary rays formed by this atom must move with a velocity greater than V. There is thus an inferior limit to the velocity of the secondary rays due to a particular kind of atom or molecule. There is, however, a superior limit to the velocity of these rays as well as an inferior one. For these rays are due to particles which move with great velocity and which were uncharged when they entered the electric and magnetic fields; they must, therefore, have been positively charged before passing through the cathode so as to be able to acquire this velocity, and then have become neutralized by combining with a negative corpuscle. The rapidly moving positively electrified particle must have attracted to itself and held bound a negative corpuscle; it cannot, however, do this if the relative velocity of the two is greater than a certain limiting velocity. This velocity is determined by the condition that it is the velocity with which a corpuscle must be moving when it has sufficient kinetic energy just to carry it away from the attraction of the positively electrified particle. The work required to separate a corpuscle from a positively charged particle may be expected to be of the same order as that required to ionize the particle when neutral. Thus, if V is the velocity of the corpuscle when it can just ionize the particle; then, if the velocity of the particle were appreciably in excess of V, a positively charged particle would not get neutralized, while if the velocity of the neutral particle were appreciably below V it would not get ionized. Hence the velocity of the secondaries which arise in the way we are considering must be very approximately equal to V, a velocity which depends only on the nature of the particle, and not on the electromotive force applied to the discharge-tube. This accounts for the fact that although the primary line may be due to particles moving with a wide range of velocities, the particles in the secondary are all moving with the same velocity.

Energy required to Ionize a Gas.—By measuring, by the method described in former papers, the velocity of the particles forming the secondary rays corresponding to any atom, we can determine V the smallest velocity with which a corpuscle must move to ionize that atom. I find this velocity for the hydrogen atom to be about 2×10^8 cm./sec., a velocity which would be acquired by the fall of a corpuscle through a potential difference of 11 volts. Hence we may take 11 volts as the measure of the energy required to ionize an atom of hydrogen.

To give to the hydrogen atom the velocity 2×10^8 cm./sec. requires a potential difference of $11\times1{\cdot}78\times10^3$ (taking $e/m=1{\cdot}78\times10^3$), or about 20,000 volts: to give the same velocity to an atom of oxygen would require $16\times20{,}000$ or 320,000 volts, a potential difference much greater than that which which we apply to our tubes. Hence we can see why the secondaries of the kind we are considering are only found with the lighter elements such as hydrogen and helium.

In addition to the secondaries which are due to the ionization of neutral atoms, there may be atoms which start with a positive charge and attract a corpuscle in their path through the electric and magnetic fields. When these fields are coterminous and uniform, these secondaries will, if the velocity is constant, be straight lines passing through the origin. If the fields are not coterminous the lines will be bent, and the bending will be complementary to that observed with the secondaries of the type previously considered. Thus, suppose the magnetic field overlaps the electric on the camera side of the observation-tube, then the rays which experience magnetic and not electric deflexions will be those which have previously travelled in their charged state all the electric and most of the magnetic field before reaching the critical region ; they will therefore have suffered a considerable deflexion, and the effect of the overlapping magnetic field will show itself in the most deflected portion of the rays, and not, as in the previous case, on the least deflected portion. Thus the curves for these rays will have the shape shown in the lower curve in fig. 4 *a* instead of that of the upper one in the same figure. If the velocities of the two kinds of rays were the same, we should have for each primary two secondaries of the kind shown in fig. 4 *a*. This disposition of secondaries is shown on many of the plates ; an example of it is given in fig. 12 (Pl. IX.).

This type of secondary, since it is produced by the combination of a positively charged particle with a negative corpuscle, might be expected to occur more readily with slowly moving particles than with fast ones : a particle moving faster than a certain velocity would not combine with a negative corpuscle, so that there would be a superior limit to the velocity of this type of secondary. There does not seem, however, any reason why there should be an inferior limit to the velocity, if the slow particles have retained their charge up to the time of entering the electric and magnetic fields ; and, as a matter of fact, this type of secondary often (as in fig. 5) shows itself as the edge of a patch of fogging on the plate rather than as a sharply defined line. There are however cases, notably with the mercury lines, where this type of secondary is more sharply defined than we should expect, and where there are, in the primary curves, particles with a smaller velocity than can be detected in the secondaries of this type.

In addition to the secondaries already mentioned, there are on many plates, for example that reproduced in fig. 14, prolongations of the primary which do not reach right up to the vertical axis but stop after going halfway. These prolongations of the primaries are parabolic and are continuations of the primary parabolas : they are therefore due to particles which in the deflecting fields have the same value of e/m as the particles which produce the primary parabolas.

The fact that the smallest electrostatic deflexion of the prolongation is just half that of the corresponding deflexion of the primary, shows that the swiftest of the particles in the prolongation has twice the kinetic energy of the swiftest in the primary ; and hence when in the electric field in the discharge-tube they have acquired twice the kinetic energy of the normal particles : they must therefore have had twice the normal charge when in the discharge-tube, but after they get into the deflecting fields the value of e/m must be normal. We infer from this that when in these fields the charge is normal ; for though we should get the right value of e/m if both the charges and the masses were doubled, the double charge would for the same kinetic energy produce double the electrostatic deflexion, and therefore for a particle with twice the normal kinetic energy would give the normal deflexion : the actual electrostatic deflexion in the prolongation is, however, only half the normal deflexion. We conclude therefore that the prolongation is due to particles which had a double charge when in the discharge-tube, but which have lost one of their charges after having passed through the cathode.

The prolongations we are considering only occur with certain types of lines. Speaking generally, they are confined to lines due to atoms as distinct from those due to molecules ; and moreover, when we find these prolongations we generally find on the same plate lines having a value of e/m twice that of the prolongations and beginning in the normal place ; these are due to the particles which have retained their double charge after passing through the cathode.

On the line due to mercury we find prolongations corresponding to particles which had three charges before passing through the cathode, and which have lost two of these charges after doing so ; the heads of these prolongations are only one-third the distance from the vertical of the normal heads. We find also on the plate lines due to mercury atoms with three charges which have retained these charges after passing through the cathode. The ability of the mercury atom to acquire multiple charges may be the reason why the parabola due to the mercury atom comes up much closer to the vertical than the parabolas due to other atoms. This is often very conspicuous : for example, the mercury line shown in Pl. IX. fig. 13 is parabolic, even when quite close to the origin.

Measurements of this curve show that some of the mercury atoms must have four or five times the kinetic energy possessed by the atoms of the other gases. It is possible that the heavy mercury atoms may linger longer in the charged state than the other atoms and last after the conductivity of the gas has become very small in consequence of the disappearance of the other atoms; then on the next break of the coil, these charged mercury atoms will be at first acted on by a much stronger electric field than that which exists when the resistance of the gas has been broken down and a considerable current passes through the tube.

On the Lines produced by the Negatively Charged Particles.—There are on the plates curves which, as the direction of the deflexions shows, are due to negatively charged particles. In one sense all these curves may be regarded as secondaries, for it is unlikely that the particles acquire their negative charges before passing through the cathode, as if they had done so they would have been retarded by the strong electric field which exists in front of the cathode. But though they are all, in this sense, secondaries, we find on examining the plates that the lines corresponding to the negatively charged particles may, like the positive ones, be divided into two types. Some of the negative lines, corresponding to the secondaries among the positives, come close up to the origin, while there are others which, like the primaries among the positives, are finite arcs of parabolas, terminating abruptly when they approach within a certain distance of the vertical axis. In fact these lines on the negative side are frequently exact reproductions in shape and size of the corresponding lines on the positive. An example of this is shown in fig. 14 (Pl. IX.), where the curves α, β are the lines corresponding respectively to the positively and negatively electrified atoms of oxygen. When the discharge passes through very pure oxygen, it will be seen that every detail in the positive curve is reproduced in the negative, including the prolongation of the parabola corresponding to the double charge. We see from this that even the fastest of the neutral oxygen atoms are able to attract and retain a negative corpuscle.

This identity in the shape of the positive and negative curves for the oxygen atoms might suggest the view that they are produced by a neutral molecule splitting up after it has passed through the cathode into a positive and a negative atom. We might be tempted to suppose that the negatively charged atoms in general arose from the dissociation of a molecule of a chemical compound in which the atom under consideration was negatively electrified, and was in combination with another positively electrified one: we might in fact suppose that we had something analogous to the dissociation of a molecule of an electrolyte in water.

Further consideration will show, however, that this view is not tenable, at any rate in a large number of cases. We find that the heads of the negative parabolas, like those of the positive, are arranged in a vertical line and that the distance of this line from the vertical line through the origin is the same as for the corresponding distance for the positive parabolas. It follows from this that the maximum value of $\frac{1}{2}mv^2/e$ is the same for the negative as for the positive particles, this quantity probably being the potential fall, V, between the negative glow and the cathode. Suppose now, to take an example, that the negatively charged hydrogen atom owed its charge to having been in chemical combination before it got through the cathode with an atom of carbon, the molecule of the compound being positively charged in the discharge-tube and acquiring a high velocity under the electric field ; after passing through the cathode the molecule gets neutralized, and then dissociates into a negatively charged hydrogen atom and a positively charged carbon one. The kinetic energy acquired by the molecule CH, if it had one charge of electricity, would be that corresponding to the fall through the potential V. Since the mass of the carbon atom is 12 times that of the hydrogen, the kinetic energy of the hydrogen atom will be that due to the fall of unit charge through a potential V/13 ; so that if this atom went through the same electric field on its way to the camera as a positively charged hydrogen atom which had been exposed in its atomic state to the electric field in the discharge-tube, it would suffer thirteen times the electrostatic deflexion of the positive one ; the photographs show, however, that they suffer the same deflexion. To explain the negative electrification of particles in this way, it would be necessary to suppose that the element with which they are combined before they are dissociated is one of very much smaller atomic weight. Hydrogen is the only element that would satisfy this condition ; and this explanation would not account for the negatively electrified particles of hydrogen itself, which are a very marked feature in the discharge. Again, if the negative electrification of oxygen were due to the dissociation of a hydrogen compound of oxygen, then for every negative oxygen atom we should have a positively electrified hydrogen one ; so that if the negative oxygen line were very strong, we should expect the positive hydrogen line to be strong also : the positives produced in this way would, however, be moving with much smaller velocities than those which had not been in combination and would therefore experience a much greater deflexion, which might be sufficient to drive them off the plate and prevent their detection. I have never been able to detect any increase in the brightness of the negative oxygen line when hydrogen was added to the gas ; indeed, the brightest negative oxygen lines I ever observed were in an exceptionally pure specimen of oxygen. It is certainly true that in some compounds of oxygen the negative lines are much more pronounced than in others. I am inclined to think that the exceptional brightness of the lines is due to the presence of the hydroxyl radicle, and that the bright lines are due to OH and not to O.

The theory which on the whole seems to me most in accordance with the observations, is that the negatively electrified particles are due to systems which are positively charged when they are in the discharge-tube ; then, after passing through the cathode, get neutralized by combining with a corpuscle, and when in the neutral condition have so strong an affinity for a negatively charged corpuscle that, in spite of the high velocity with which they are moving past it, they are able to capture a corpuscle and thus become negatively electrified. This attraction for the negative corpuscle depends on the chemical properties of the atom. The atoms of some elements do not exert sufficient attraction to enable them to become charged in this way : for example, I have never observed any indications of negatively charged helium, argon, nitrogen, or mercury, however strong the lines corresponding to the positively charged atoms may have been. On the other hand, the atoms of hydrogen, carbon, oxygen, sulphur, chlorine are conspicuous for the readiness with which under ordinary conditions they acquire a negative charge. The case of oxygen is especially interesting. In very pure oxygen, carefully dried by liquid air, the oxygen occurs on the negative side solely in the atomic condition : an example of this is shown in fig. 14, where the only line on the negative side is one due to atomic oxygen. If, however, a small quantity of hydrogen, say from 1 to 3 per cent. by volume, is added to the oxygen, another line appears on the negative side with a value of m/e about 33 times that for the hydrogen atom ; an example of this line is shown in fig. 15 (Pl. IX.).

It is remarkable that this line disappears again when the quantity of hydrogen is increased, with 20 per cent. hydrogen it is no longer visible. I have a series of about 40 photographs of the discharge through mixtures of hydrogen and oxygen in varying proportions ; in all of these, where the quantity of hydrogen is small, the line is visible, but unless the oxygen is greatly in excess it is invariably absent. I ascribe this line to the formation of H_2O_2. The question whether the actual carrier of the negative electricity is the molecule H_2O_2, or HO_2, or even O_2, is difficult to determine, as the lines are not strong enough to allow of the very finest tubes through the cathode being used. The following are the values of m/e obtained for this line on different plates, the value of m/e for the hydrogen atom being taken as unity:—33·5, 35, 33, 35, 32, 33, 33·5, 34, 35, 33, 32, 31; mean 33·3. This suggests that the carrier of the negative charge is not O_2 but either HO_2 or H_2O_2. The stronger negative line, with a value of m/e near 16, is, I am inclined to think, when hydrogen is present, not O but OH, as the measurements of this line on plates, taken with mixtures of oxygen and hydrogen, uniformly gave values of m/e slightly greater than 16. If the hydroxyl radicle is the carrier for this line, we can understand why the line is especially bright when the discharge passes through the vapours of some organic compounds, such as methyl alcohol, when the hydroxyl radicle is very likely to be liberated in the process of ionization. Though the line 33 only appears in mixtures of hydrogen and oxygen when the oxygen is greatly in excess; it appears in mixtures of ethylene and oxygen even when only a small quantity of oxygen is present.

The negative lines which appear when the discharge passes through the vapours of hydrocarbons are interesting. When there are no bonds between two atoms of carbon, as for instance in marsh gas, carbon monoxide, or carbon dioxide, the only line on the negative side which can be ascribed to carbon is the line for which m/e is 12, which is in general very bright. When, however, we take compounds in which there are bonds between the carbon atoms, such as ethylene and acetylene, we frequently find that in addition to the line for which $m/e=12$ there is another for which m/e is about 24, showing that we have a system with a strong affinity for negative electricity formed from two carbon atoms, with perhaps one or two atoms of hydrogen. When the discharge passes through benzene vapour we get in addition to the lines 12 and 24 a line near to 36; and I have sometimes thought that I could detect one near 48, though this is exceedingly faint: thus we can get strongly electronegative radicles containing three or more atoms of carbon. In very carefully purified helium the negative lines due to impurities are exceedingly faint, much fainter than they are in other gases. On one or two plates I have observed a negative line for which m/e was about 22.

On the way the Positive Rays are produced.—One very remarkable feature of the photographs is the length of some of the arcs of the parabolas, the horizontal deflexion of the end of the arc being often a large multiple of that of the beginning. Since the kinetic energy possessed by the particle is inversely proportional to its horizontal deflexion, this result shows that the kinetic energies of particles having the same value of e/m vary within wide limits. Assuming that the kinetic energy of the particle is due to the action upon it when in the dark space of the electric field, we might get this variation in the kinetic energy :—

1. If the charged particles all started from the same region, the end of the dark space, but before reaching the cathode got neutralized and so were only under the action of the electric field for a fraction of the journey through the dark space.
2. If the ionization which produced the positive rays occurred not merely at the end of the dark space, but to some extent throughout the whole of this space.
3. That the small amount of kinetic energy possessed by some of the particles is due to their colliding with the molecules of the gas whilst passing through this space, and in this way losing some of their kinetic energy.

Let us begin with the first of these suggestions. We know by direct experiment that unless the pressure is very low the rays after they pass through the cathode get neutralized and lose their charge for a time, sometimes acquiring it again by being ionized by the collisions they make. If this process went on in front of the cathode as well as as behind it, we should get variation in the kinetic energy of the positive rays, as some of them would have passed a larger fraction of their time than others in the uncharged state, when in the electric field. I do not think that this explanation is the true one, for the reason that the conditions in the dark space differ essentially from those which prevail after the particles have passed the cathode ; there is no electrical field after passing the cathode, so that the relative velocity of the positive rays and the corpuscles with which they are to combine is merely the velocity of the positive rays themselves. In the dark space in front of the cathode there is an intense electric field in which the corpuscles are moving far faster than the positive rays, so that the relative velocity of the positive rays and the corpuscles is very much greater than on the other side of the cathode. Thus the union of a positive ray and a negative corpuscle is far less likely to occur in the dark space than when the positive ray has passed through the cathode.

The third suggestion, that the loss of kinetic energy is due to collisions between the positive rays and the molecules through which they are moving in the discharge-tube, is open to the objection that it would produce effects of the same general character on all the lines on the plate. As a matter of fact, however, we find that some of the lines, notably those of compounds formed by the action of the electric discharge when it passes through mixed gases, are quite short, showing that all the rays have much the same kinetic energy. On the other hand, many of the lines are long and of nearly equal intensity along the whole of their length; while frequently abrupt alternations of intensity occur along the lines, giving them a beaded appearance. It is remarkable that this beading may occur on some lines, while other lines on the same plate are free from it.

The second explanation seems to me to be the most probable one, viz., that the positive rays are produced at different places in the dark space, and so fall through different potential differences and acquire different velocities.

One of the most striking things brought to light by the photographs is the extent to which the molecules of the gas filling the tube are broken up by the electric discharge. The dissociation which occurs in the gas is far greater than that required to make the gas a conductor of electricity; for all that would be required for this purpose would be for some of the molecules to lose a corpuscle and thus become positively charged: these would be able to carry the positive electricity, while the negative could be carried by the corpuscles or by molecules on which corpuscles had settled; a process of this kind would not involve the disintegration of molecules into atoms. The photographs show, however, that something much more complicated than this goes on in the dark space and the negative glow, for on all the photographs there are lines indicating atoms as well as those corresponding to molecules, and instead of there being only one type of carrier for the positive electricity, there are in general a considerable number of types, for example in benzene vapour I have counted seventeen different types of positive carriers.

Indeed, the splitting up of the gas by the electric discharge is so complete that the photographs of the positive rays obtained from the vapours of different hydrocarbons may be almost identical. Thus, for example, the prominent lines for the vapours of methyl alcohol, ethyl alcohol, ether $(C_2H_5)_2O$, and dimethyl ether are identical, showing that the more important rays are due to the products of dissociation of the molecules of these substances, and not to the undissociated molecules ; the lines due to the latter, if they occur at all, are exceedingly faint.

On the Relative Brightness of the Lines on the photographic plate as an index of the number of the Carriers producing the Lines.—It is necessary, however, to be very careful in drawing any conclusion as to the number of carriers having any particular value of e/m from the brightness of the parabola corresponding to this value of e/m. When the kinetic energy of the particles of different kinds is the same, the photographic plate is much more sensitive to the lighter carriers with a high velocity than to the slower and heavier carriers. I had suspected that this was the case for some time, but had no idea that the effect was so marked until I compared the indications of the plate with those of a Faraday cylinder.

The details of the apparatus used for the Faraday cylinder will be described later : it will be sufficient to say here that they were such that the particles forming the different parabolas could be driven in succession into the Faraday cylinder, and the charges they communicated to it in a given time measured. As these charges (when the particles only carry one unit charge) are proportional to the number of particles entering the cylinder, the indications of the Faraday cylinder will give the number of the different kinds of particles. For example, when the gas in the discharge-tube was the residual gas left after the air was pumped out, the lines on the photographic plate due to the hydrogen atom and the molecule were very much brighter than that due to the oxygen atom, and the line due to the hydrogen atom than that due to the molecule. The experiment with the Faraday cylinder showed, however, that there were many more atoms of oxygen than of hydrogen, and also that there were more hydrogen molecules than atoms. Again, when the tube contained pure oxygen the line on the plate due to the oxygen atom was brighter than that due to the oxygen molecule ; the Faraday cylinder showed, however, that there were many more molecules than atoms carrying the discharge. In all cases, it is the lighter atoms which produce an effect on the photographic plate greater than is warranted by their number. I think the explanation is that these particles only penetrate a very short distance into the film, and so can affect only a very small amount of silver, the faster particles penetrate more deeply into the film than the slower ones ; there is thus more silver at the disposal of the quick particles ; in other words, the film is more sensitive to quick particles than to slow ones.

The discrepancy between the number of rays of a particular kind and the intensity of the effects they produce is even more marked in the phosphorescence they excite in a willemite screen than the impression they produce on a photographic plate. With a willemite screen I have found that the brightness of the line due to the hydrogen atom may be very much greater than that due to the oxygen molecule when the Faraday cylinder method showed that there were 300 times as many positively charged molecules of oxygen as there were atoms of hydrogen. I think we may get an explanation of this, if we consider the mechanism by which ionization may be imagined to be produced. When a molecule is ionized by a negative corpuscle, the corpuscle has to possess a finite amount of energy. Let us suppose for the sake of clearness that the energy required is that due to a fall of the atomic charge through 10 volts; this corresponds to a velocity of the corpuscle of $1{\cdot}9 \times 10^8$ cm./sec., and we may suppose that to enable a corpuscle to escape unattended from a neutral atom, it must have a velocity of this order. If this velocity is to be communicated to it by collision with another body, that body must be moving with a velocity comparable with that acquired by the corpuscle.

Now in the case of the positive rays it is only in general the lightest atoms and molecules, the atom and molecule of hydrogen and the atom of helium, which possess velocities as high as this, and it is therefore only these rays which can produce ionization of the type of that produced by cathode particles. The heavier particles, though possessing far greater energy than that due to a fall through 10 volts, are moving much too slowly to impart by collision to a particle a velocity as great as $1{\cdot}9 \times 10^{-8}$ cm./sec. By sending these heavy particles between parallel plates maintained at different potentials and measuring the current sent across the plates, I have found that these heavy particles can produce a very considerable amount of ionization. The question arises, how is this ionization produced? The negatively electrified corpuscle must, in order to escape from the attraction by which it is bound to the atom, possess a certain amount of kinetic energy; this, if the mass is as small as that of a corpuscle, requires it to have a very high velocity. One method by which a comparatively slow positive ray might start off a corpuscle at a high speed is considered on p. 235 when we discuss the difference between ionization by cathode and positive rays. Again, if the corpuscle were firmly attached to a very much greater mass, this system could possess the requisite amount of energy with a very much smaller velocity, a velocity no greater than that possessed by the heavier positive rays, and which these rays could communicate to the system by colliding against it. This method of ionization might occur in a compound molecule if the negative charge clung, say, to an atom of oxygen, while it would not occur if the atoms were uncombined, when there would be no body of a mass comparable with that of an atom for the corpuscle to cling to. There are some phenomena which strongly suggest some process of this kind. For example, when the liquid alloy of sodium and potassium is bombarded by positive rays, it is only the specks of oxide on the surface which give out the sodium lines, the clean parts of the surface are quite dark. On the view just given this arises from the atom of oxygen being knocked off the atom of sodium with which it is combined and carrying off a negative charge, leaving the atom of sodium positively electrified, and in a condition to give out its spectrum: with the pure metal this process does not occur. There are some phenomena connected with the luminosity of flames which are also in accordance with this idea.

The great sensitiveness of willemite to cathode rays and to fast positive ones, and its inertness under the slower positive rays, would on this view be due to its luminosity being mainly produced by ionization of the type due to particles which have a velocity of the order 2×10^8 cm./sec.: velocities of this magnitude are possessed by the atoms of hydrogen and helium and the molecule of hydrogen, but not by the other atoms in an ordinary discharge-tube.

The fact that on the photographs the intensity of the lines due to particles of different kinds is not proportional to the number of particles which produce the lines, prevents us from drawing conclusions from the inspection of the photographs as to numbers of the various types of carriers of positive electricity present in the positive rays, and indeed would very often convey a wrong impression. Thus, for example, in a number of photographs I possess of the rays passing through mixtures of hydrogen and oxygen in varying proportions, the relative brightness of the lines of hydrogen and oxygen shows but little relation to the relative quantities of these gases present in the mixture. When, however, the numbers of particles in these lines were measured by directing them in succession on to the slit of a Faraday cylinder and measuring the charge received in a given time by the cylinder, it was found that the relative number of particles in the hydrogen and oxygen lines varied directly as the relative number of hydrogen and oxygen molecules present in the mixture.

The relative number of the different kinds of particles present in the positive rays is a quantity of fundamental importance for the consideration of the chemical changes which go on in the gas in the discharge-tube; this quantity is being measured in the Cavendish Laboratory by receiving the particles separately on a Faraday cylinder and measuring the charge received by the cylinder. The results of these measurements will be given in a separate paper.

Though the photographs do not give accurate quantitative estimates of the numbers of the different particles, they do give some very interesting results as to the processes at work in the ionization of the gases. Thus on some photographs the line due to an atom of, say, hydrogen was stronger than that due to the molecule, while on others the line due to the molecule was the stronger. Another interesting and in my opinion very suggestive result, comes to light from an inspection of the plates taken when the discharge passed through mixtures of hydrogen and oxygen. It is illustrated in figs. 17 & 18 (Pl. IX.) and also in figs. 21 *a,* 21 *b*, & 21 *c*. In the plates from which these figures were made there were very pronounced differences between the appearance of the lines due to the hydrogen atoms and those due to the hydrogen molecule. These differences may be of various kinds: for example, in fig. 17 the line due to the hydrogen atom is of uniform intensity throughout, while that due to the molecule is very weak at the head but intense elsewhere; in others the line due to the atom is uniform, but that due to the molecule is much more intense at some places than at others, thus having a beaded appearance. In others again (fig. 18) the line due to the atom is of uniform intensity, while that due to the molecule is very thin at the head and remains so for some distance, and then develops great intensity. The point, however, on which I wish to lay stress is that *when there are such differences between the lines due to the atom and molecule of hydrogen, there are similar differences between the lines due to the atom and molecule of oxygen.* In other words, that all the atomic lines have common characteristics, as have also all the molecular lines, but that these characteristics are frequently quite different. A similar effect can be observed in mixtures of hydrogen and nitrogen, and indeed in all the mixtures I have tried. As a general rule, the intensity along the lines corresponding to the atoms is more uniform than that along the lines corresponding to the molecules: the uniformity of the atomic line is especially marked in the lines corresponding to atoms with two charges, such as C_{++} N_{++} O_{++}. It is also noteworthy that on the lines corresponding to the monatomic elements helium and mercury we get a blending of the characteristic features of both the atomic and the molecular lines.

The difference between the atomic and the molecular lines suggests that the charged atoms and the charged molecules are produced by different processes ; that in fact there is more than one process of ionization at work, and that the process which produces the charged atom is different from that which produces the charged molecule. We have in the discharge-tube rapidly moving cathode particles moving away from the cathode, and positively electrified atoms and molecules moving towards it; each of these systems can, as is well known, produce ionization by collision. With regard to the ionization due to the cathode rays, there are several reasons for thinking that in the dark space itself this is not considerable. For if a cathode ray, starting from the cathode, produced on an average in its course through the dark space another corpuscle, this second corpuscle would, under the influence of the strong electric field which exists in that space, acquire a considerable velocity, though not of course so great a one as that of a particle which had started from the cathode and passed through the whole of the dark space. There would thus be a considerable range of velocity in the beam of cathode rays emerging from the dark space, and no approach to a condition where all the cathode rays in the bundle are moving with the same velocity. Now, although it is true that the cathode rays produced in a discharge-tube are not all moving with absolutely the same velocity, yet at the pressures at which these experiments on positive rays were made (of the order of 1/300 of a mm.), the variation in the velocities are not large, by far the larger portion of the particles having velocities which do not vary in value by more than a few per cent. So that we may conclude that the larger part of the positive ions which are produced by the cathode rays are produced beyond the dark space, and drift into this space under the action of the feeble electric forces which are found in the negative glow and the positive column.

We have data which confirm this idea. Glasson has shown (Phil. Mag. October 1911) that cathode rays with a velocity of $4\cdot7\times10^9$ cm./sec. moving through air at a pressure of 1 mm., produce 1·5 pairs of ions per cm. of path. These are comparatively slow cathode particles ; in our experiments the velocity of the cathode particles when they left the dark space was considerably greater than this ; and as the ionization due to cathode particles varies inversely as the square of the velocity, the ionization at the same pressure would be less than that found by Glasson. In our experiments, the pressure of the gas through which the particles passed was only about 3/1000 mm. Hence, if we left out of account the diminution in the ionization due to the increase in velocity, the cathode rays would only produce about 1·5 pairs of ions in a path of 333 cm. This distance is much greater than the width of the dark space. This confirms the conclusion that in the dark space itself the number of positive ions produced by the cathode particles, and therefore the number of positive rays arising in this way, would only be a small fraction of the number of cathode particles starting from the cathode.

Let us now consider the ionization due to the positive particles themselves. Direct measurements show that these, when they have passed through the cathode, produce ions at the rate of a pair of ions for a centimetre or so of their path through air at a pressure of 3/1000 mm.

Thus for the same number of rays the ionization due to positive ones would be greater than that due to cathodic ones : it is probable, however, that the cathode particles are much more numerous than the positive rays. For we know that when a positive ray strikes against a metal plate such as the cathode of a discharge-tube, the plate emits negative particles. Now the energy of a positive ray when it hits the cathode is very much greater than the energy required to liberate a negative particle; so that as far as energy is concerned the positive particle has ample store for liberating a considerable number of negative particles. We have indeed direct evidence that it actually does so; for Füchtbauer (*Phys. Zeit.* vii. p. 153) found that when positive rays, produced in a tube with a potential difference of about 20,000 volts between the anode and cathode, fell on a plate of aluminium, the number of cathode particles ejected from the plate was about four times that of the positive particles falling upon it. We should therefore expect the number of cathode particles starting from the cathode to be considerably greater than the number of positive particles arriving at it; this would imply that the greater part of the current through the tube is carried by the cathode particles. So that though the ionization produced by one cathode particle may be less than that due to one positive one, the excess of cathode particles over positive may make the total number of ions produced by the cathode particles comparable with that produced by the positive. In consequence, however, of the much greater speed of the negative corpuscles, their density will be less than that of the positive, so that there is at any time in the dark space an excess of positive electricity.

The positive rays have been shown by Füchtbauer (*loc. cit.*) and Austin (Phys. Review, xxii. p. 312) to be reflected to some extent when they strike against a plate of metal; *i. e.*, some of the rays rebound from the cathode without giving up their charge of electricity; after rebounding, they will be again attracted to the cathode by the electric field and have a second opportunity of communicating their charge to it. This rebound of the positive rays will increase the density of the positive electrification near the cathode, while it will diminish the current carried by the positive rays below the value calculated on the assumption that all the positive rays give up their charge to the cathode the first time they strike against it. The density of the positive electrification near the cathode will therefore be greater than the value deduced on the assumption that the current carried by the positive rays is equal to the density of the positive electricity multiplied by the velocity which a positive ion would acquire under the electric field in its journey from the place where it originated to the cathode. This I think may be the explanation of an important point to which Mr. F. W. Aston has called attention: this point is that, even if we suppose the whole of the current through the tube to be carried by the positive electricity (we have seen that probably only a fraction is), then the density of the positive electricity calculated on this assumption is far too small to be consistent with the equation

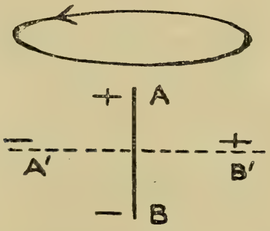
$$4\pi\rho=\frac{dX}{dx},$$

where ρ is the density and X the electric force in the neighbourhood of the cathode.

The reflexion of the positive rays involves the presence near the cathode of a number of positive ions with comparatively small velocities. As close to the cathode the cathode rays are also moving slowly, they would be able to combine with slowly moving positive particles, and thus give rise to the luminosity which is to be seen close to the cathode.

On the Difference in the kind of Ionization produced by Cathode Particles and by Positive Rays.—We have seen that on the photographs there are sometimes marked differences between the lines due to the atoms and those due to the molecules. This suggests that the atoms and the molecules get their charges in different ways. It seems, on *a priori* grounds, that we should ascribe the formation of the atoms mainly to ionization produced by positively charged atoms or molecules. For at the end of their paths in the cathode dark space these have in our experiments energy represented by the fall of the atomic charge of electricity through a potential difference of more than 20,000 volts. This is thousands of times the energy developed per molecule in any chemical reaction. It is therefore probable that when a charged particle of atomic mass collides with another atom, it will give to it sufficient energy to tear it from any compound, and therefore produce dissociation. We should expect therefore that the fast positive rays would disintegrate into atoms any molecules against which they struck. On the other hand, a fast cathode particle would be able to penetrate into the atom, and would collide rather with individual corpuscles than with the atom as a whole. We should expect then that in general the result of such a collision would be to detach a corpuscle from the molecule without necessarily splitting it up into atoms. The question arises, if the molecule were split into atoms by the impact of the positive rays, would these atoms be positively charged, or would when the atoms split off some be charged positively, others negatively? or, as a third alternative, would they be uncharged when liberated and acquire a positive charge by subsequently colliding with cathode rays? The evidence at present before us points to the conclusion that an overwhelming majority of these charged atoms have positive charges, *i. e.* have lost a corpuscle: has this corpuscle been detached by the impact with a positive particle which set the atom free? To force a corpuscle from an atom would seem to require the communication to the corpuscle of an amount of energy equivalent to that possessed by the corpuscle when it has a velocity comparable with 2×10^8 cm./sec. It is difficult to see how a comparatively slowly moving heavy atom could communicate so great a velocity to the corpuscle directly. It might, however, liberate a corpuscle which was previously moving with this velocity in a state of steady motion round a massive system. Take, for example, the following case: Suppose a corpuscle were moving in a state of steady motion round an electrical doublet A B, fig. 19, having a mass comparable with that of an atom; suppose, now, that the doublet were struck by an atom and knocked into a position A′B′ at right angles to AB. The corpuscle would fly off with the velocity it had before the impact with the doublet: and it is easy to show that the work required to turn the doublet from AB to A′B′ is equal to the energy with which the corpuscle flies off. We see that in some such way as this a slowly moving atom with the requisite energy might detach a corpuscle from an atom.

Fig. 19.



Atoms with double charges.—The photographs show that the atoms of nearly all the elements, with the very suggestive exception of hydrogen, occur with two charges, though the number of these doubly charged atoms is always small compared with those having a single charge. We are able to detect the double charge on the atom because the parabola corresponding to the doubly charged atom is distinct from that due to the singly charged atom or molecule. We could not in this simple way detect the existence of doubly charged molecules, because the parabola corresponding to the doubly charged molecule would coincide with that due to the singly charged atom. We can, however, indirectly get some evidence on this point. Some of these doubly charged systems lose one of their charges before passing through the electric and magnetic fields: they are deflected by these fields into the parabola corresponding to the singly charged atom; but inasmuch as they had when in the electric field in the dark space a double charge, they will have acquired when in that field twice the kinetic energy of a singly charged atom. They will therefore occur on the parabola at a position which is only half the distance from the vertical line of that occupied by the atoms which have had a single charge during the whole of their career. The effect of this is to make the parabolic arc corresponding to the atom have a kind of beak. An example of this is shown in fig. 14 (Pl. IX.). Sometimes this prolongation of the parabola is of nearly uniform intensity, as in fig. 14; in other cases it is much brighter at the tip than at any other position, giving the curve a beaded appearance. Now it is remarkable that this prolongation of the parabolic arc towards the vertical axis occurs, as far as my experience goes, only on the lines corresponding to the atoms, and not on those corresponding to the molecules: this I think shows that the ions with double charges are atoms and not molecules. I have not observed on the plates any indications of molecules with two charges. Another question as to which we can get some information from the plates, is whether the doubly charged atoms get their double charge at one collision, or whether they get one charge at one collision, and the other at a subsequent one. If it took two collisions to give them the two charges, then we should expect that the number of these particles with an amount of energy approximately that due to the fall of the double charge through the whole of the dark space would be small compared with that of those which had a smaller amount of energy. For consider the condition which must exist for the particle to have the maximum kinetic energy: the two collisions which cause it must occur close together at the boundary of the dark space away from the cathode. Compare this with the region open for collisions which ionize the gas so that it falls into the cathode with about half this kinetic energy. Then, if the first collision occurs near the boundary of the dark space, a second collision near the cathode will be required, but the particle in this case is not obliged to make the first collision close to the boundary—it can go some way before making the first collision, and then make up for the loss of energy caused by the delay in making the first collision by making the second collision a little earlier. There is thus a much wider scope for adjustment in this case than in the previous one; and we should expect the number of particles with approximately half the maximum kinetic energy to be large compared with the number having nearly the maximum. As a matter of fact, however, the lines corresponding to the doubly charged atoms are conspicuous by the uniformity in their intensity. This is inconsistent with the ionization occurring in two stages; and we conclude that in some of the collisions which produce the charged ions the conditions are such that the ions receive a double charge.

Beading in the Molecular Lines.—We have seen that the possibility of double-charged ions gives a beaded appearance to the atomic lines, the beads appearing nearer the vertical line than the main portion. The molecular lines do not show this type of beading, but they show frequently another type in which the beads, instead of being nearer the vertical axis than the head of the parabola, are further away from it. A conspicuous example of this is shown in fig. 21 *b*, in which the larger quantity of the molecules of hydrogen and oxygen occur after the first beading. Sometimes, as in figs. 16 and 16 *a*, there are several sets of beads following each other at short intervals. The only atoms in which I have observed clear indications of this type of beading are those of the monatomic gases helium and mercury vapour, and for these gases there is no distinction between the atom and the molecule, so that this does not form an exception to the rule. This kind of beading depends very much on the position of the cathode in the discharge-tube and its shape. With some cathodes I have never observed them; with others I have found them when the cathode was in one position, not when it was in another. I think these are due to the impact of the cathode rays against the walls of the glass giving rise to slow secondary rays of great ionizing power. A slight inclination of the cathode might cause the rays to hit a portion of the discharge-tube which previously escaped, and thus start secondary rays nearer to the cathode, which would produce ions reaching the cathode with smaller energy than those which started from the negative glow.

It is remarkable that on many of the plates the head of the first beading on the molecular line is just twice the distance from the vertical of the head of the parabola, showing that the particles in the first beading have fallen through a potential difference just half of that fallen through by the particles at the head of the parabola. This is not, however, always the case ; if it were, we should have to look for an explanation of this beading to some other cause than that just given. If, for example, aggregates of two molecules were formed possessing a single charge, and if, after passing through the cathode, the two molecules separated, one retaining the charge and the other going on uncharged, then the charged molecule would have half the energy due to a fall of the atomic charge through the electric field in the dark space, and would therefore be at the point often occupied by the first beading. If this were the explanation we should expect to find traces of the aggregates which had not broken up on passing through the cathode : these would be on a parabola corresponding to a value of e/m half that of the molecule. I have never been able to find traces of such parabolas. Again, it is not clear on this view why the existence of this beading should be so dependent on the shape of the cathode and its position in the discharge-tube. For this reason I am inclined to regard the ratio of 2 to 1 which sometimes exists between the horizontal distances of the first bead and the head of the parabola as accidental, and to prefer the first explanation of this beading.

Beading of the Mercury Line.—The beading on the mercury line is especially well marked since, as mercury is monatomic, the atomic as well as the molecular beadings occur on this line. As the mercury atom occurs with three charges, we get on the mercury line ($m/e=200$) beads corresponding to the atom which was highly charged when in the dark space, but lost two of the charges after passing through the cathode. As the kinetic energy acquired by the triply charged atom in the dark space is three times that acquired by the singly charged atom, the head of the bead corresponding to the triple charge will only be $\frac{1}{3}$ of the distance from the vertical of the head of the main portion of the parabola. This would bring the mercury parabola much nearer to the vertical and to the origin than the other parabolas. Now it is a very remarkable feature of the mercury parabola that it very often seems to reach right up to the origin, as, for example, in fig. 14. Measurements show that this is a parabola up to quite close to the origin : if this is so, then some of the particles must have acquired an amount of kinetic energy very large compared with that acquired by the fall of the atomic charge through the potential difference in the dark space. From the appearance of the curve a triple charge would hardly be sufficient to account for the close approach to the origin. Can it be that some of the mercury ions linger on from one discharge of the induction-coil until the next, and thus get exposed to the intense field which acts on the gas in the early stages before the normal discharge is established?

Besides the ionization due to the collisions with the positive and cathode particles, there must be some due to the "Entladungstrahlen" which are emitted from the negative glow as well as from the Röntgen rays which are produced when the cathode rays strike against the walls of the tube. At these low pressures there would be little absorption of such rays by the gas in the tube, so that the ionization due to this source would be uniform throughout the dark space. We are at present without the data which would enable us to estimate what proportion of the ionization is due to these rays and what to ionization by collision. The Röntgen rays, when they strike against the cathode, cause it to emit negative corpuscles. Now the experiments of Mr. Whiddington and others show that the velocity of the corpuscles ejected when Röntgen rays fall on a metal plate is approximately the same as the velocity of the cathode rays which produce them. If we apply this to the case of the discharge-tube, it indicates the existence of two streams of cathode particles, one due to the impact of the positive particles which emerge with comparatively small velocities (the experiments of Füchtbauer and myself indicate that this velocity is comparable with that acquired by the fall of a cathode particle through a potential difference of between 20 and 30 volts); and another stream due to the incidence of the Röntgen rays which emerge with a velocity comparable with that due to the potential difference between the anode and cathode in the discharge-tube, which amounts to many thousands of volts. The comparative homogeneity of the stream of cathode particles shows that the production of cathode particles by these two methods cannot be comparable in importance. Indeed, it would seem that any preponderating production of these particles by the second method would lead to instability in the discharge, for the ejected particle would start with a velocity comparable with that due to the whole electric field; it would in its course through the dark space increase this velocity; the Röntgen ray it produced at the end of its course would eject from the cathode cathode rays with a higher initial velocity than their parent, and the process would go on evidently leading to instability. If even an appreciable fraction of the cathode particles were ejected from the cathode by this method, we should expect to find in the cathode stream sets of cathode particles, α_1, α_2, α_3—moving more rapidly than the main body of these particles, and such that the energy possessed by an individual particle in the set α_2 exceeded that possessed by one in α_1 by the energy acquired by a cathode particle in falling through the dark space, while the energy of one in set α_3 exceeded that of one in α_2 by the same amount, though the number of particles in α_2 would be much smaller than that in α_1, and the number in α_3 still smaller than in α_2, and so on. As we have no evidence of the existence of a spectrum of this kind in the cathode rays, I think we must conclude that practically the whole of these rays are produced by the positive ions.

The smallness of the electric force at the end of the dark space is responsible, I think, for the luminosity in the negative glow, for when the field is strong, as in the dark space, the corpuscles and positively charged atoms and molecules acquire such great velocities that they rush past each other without combining. When, however, this field vanishes, positive and negative particles may only have small relative velocities and combine and give out light in the process. It is in the negative glow that we must look for new compounds formed by the union of atoms dissociated by the discharge.

Chemical Compounds produced by the Electric Discharge in Gases at very low Pressures.—The study of the positive rays has revealed the existence of some compounds which have not hitherto been detected by chemical methods. The measurement of m/e for the lines on the plate gives us the molecular weight of the carrier producing the line, or of some submultiple of it if the carrier is charged with more than one unit of electricity. In some cases this leads to the identification of the line without difficulty ; in other cases more than one kind of carrier might give the right molecular weight : for example, if we found a carrier having a molecular weight 28 it might be N_2, CO, or C_2H_4 : in such cases further experiments are necessary. If it was found, for example, that the line was absent when nitrogen had been very carefully eliminated from the gas, there would be a strong presumption that the line was due to the nitrogen molecule. By observing the behaviour of the line when the gas in the discharge-tube is varied, we can often determine without ambiguity the gas to which it is due.

I shall in what follows confine myself to the consideration of lines which satisfy both the tests for a primary line given on page 217. There are several lines satisfying the first of these tests which cannot be explained by any known substance ; but as I do not feel sure that the possibility of their being secondaries is excluded by this test, I shall not base any conclusions upon them. There is a strong one corresponding to an atomic weight 6 in fig. 20 (Pl. IX.) taken with a mixture of helium and hydrogen.

Existence of H_3.—On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which $m/e = 3$ has been detected. There can, I think, be little doubt that this line is due to H_3, and not to the carbon atom with four charges; for if it were due to carbon we should expect to find it conspicuous in carbon compounds, which it is not, and it would be accompanied by the lines due to the carbon atom with 1 and 2 charges, both of which are easily developed. These do not, however, accompany the line under consideration.

The line m/e does not occur, as far as we know, in absolutely pure hydrogen, but if a trace of air or oxygen is added to very pure hydrogen, the line appears under certain conditions of pressure and current.

Copies of photographs of plates showing this line are given in figs. 21 *a*, 21 *b*, and 21 *c* (Pl. IX.) ; the line is the one marked α ; above it are the lines due to the hydrogen atom and molecule. The other lines on the plate are due to the oxygen atom and molecule and to the mercury atom. The existence of this substance is interesting from a chemical point of view, as it is not possible to reconcile its existence with the ordinary conceptions about valency, if hydrogen is regarded as always monovalent. The polymeric modification of hydrogen seems to require special conditions for its formation, for it cannot be detected on many of the plates taken with hydrogen in the tube.

Formation of N_3 *or* N_3H *by the Discharge.*—When the discharge passes through nitrogen at not too low a pressure, a strong line is found for which m/e is about 43, the numbers ranging from 42 to 44. This value of m/e is about the most embarrassing one there is for the application of this method of analysis, for there are many compounds which might occur in the tube which have values of m/e equal or nearly equal to 44. CO_2 for example, a common impurity in the tube, has a molecular weight 44 and would give a line in this region, and one test for the presence of CO_2, the existence along with it of CO, cannot be applied in the case of the discharge through nitrogen, as N_2 has the same molecular weight and would of course be present. N_2O has again the molecular weight 44, and might be formed if oxygen were present, and NO_2 has a molecular weight 46. We have, therefore, to apply further tests before we can identify this line. If the line were due to CO_2 present as an impurity, it is difficult to see why the presence of nitrogen should make the line so much stronger. Again, if it were due to CO_2, the oxygen lines would be found, as these are readily developed on both the positive and negative sides when oxygen, free or combined, is in the tube. But on some of the plates, when great care had been taken to get rid of oxygen, the line under consideration was strong while the oxygen lines were too faint to be detected. This is unfavourable to the view that the line is due to CO_2 or N_2O, and leaves us with N_3 and N_3H as alternatives. The hydrogen lines were present on all the plates, as, indeed, they always are, but I could not detect any increase in the intensity of the line under consideration when a considerable amount of hydrogen was mixed with the nitrogen. I am inclined, therefore, to regard the line as due to N_3 and not to N_3H. This line is not nearly so strong as the line due to the nitrogen atom, and, judging from the evidence afforded by these photographs, I should be inclined to attribute the "active form of nitrogen," investigated by Professor Strutt, to atomic nitrogen rather than to N_3. It is interesting to find that in the discharge-tube nitrogen exists in an exceptionally large number of modifications. N_{++}, N_{+}, N_{2+}, N_{3+} are found on all plates when the tube contains nitrogen, and on one or two plates I have found a line with $m/e=4{\cdot}7$, which I attribute to N_{+++}. I have never found a line corresponding to nitrogen with a negative charge.

On some Lines observed when the Discharge passes through mixtures of Hydrogen and Oxygen.—We have already alluded to the negative line in the neighbourhood of $m/e=32$ when the discharge passes through oxygen containing a small proportion of hydrogen. There is also a line on the positive side with a value of m/e about 50; its occurrence is not, as in the case of the negative line, limited to those mixtures which contain a small quantity of hydrogen; it occurs in all mixtures. I have not found it, however, in very pure oxygen. The most natural origin of the line would be ozone. Against this, however, is to be set the fact that it does not occur in pure oxygen; if it is not ozone, the alternative seems to be H_2O_3.

With mixtures of hydrogen and oxygen we get the water line, $m/e = 18$, and sometimes a faint line for which m/e is about 20; the compound H_4O would satisfy this condition.

With pure oxygen, or with a large excess of oxygen, the mercury lines disappear, owing I suppose to the combination of the oxygen and the mercury vapour. With new aluminium cathodes I have found that, whatever be the gas in the tube, the mercury lines are either absent or very faint; they attain, however, considerable strength after the tube has been used for some time and the electrodes have got saturated with mercury vapour.

When the discharge passed through CS_2, I found the line $m/e = 44$ very strong; this, I think, is due to the new compound CS discovered by Sir James Dewar and Mr. H. O. Jones. Special precautions have to be taken in this case, as CO_2 gives the same line; oxygen was carefully excluded, without affecting the strength of the line, and in this case the line due to CO was exceedingly faint. This is a very searching test, as when CO_2 is in the tube, the line due to CO is always very strong, generally stronger than the one due to CO_2 itself.

The ammonia line was found when mixtures of nitrogen and hydrogen were in the discharge-tube.

It is quite possible for an element to be in the tube without producing its line on the photographic plate. Thus I made a number of experiments with nickel carbonyl in the discharge-tube with the object of determining the atomic weight of nickel by this method, but I was never able to detect a line corresponding to nickel *.

Again, when zinc ethyl is in the tube, I have never been able to detect the zinc line.

Indeed, with the exception of mercury vapour, the lines due to heavy molecules or atoms are not so conspicuous as we might expect. I attribute this to the peculiarities of the photographic plates, which seem much more sensitive to rapidly moving light atoms than to heavy ones with the same amount of energy but a smaller velocity.

As the photographic method, although excellent for detecting the existence of different substances in the discharge-tube, is not suitable for quantitative measurements of their

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* Since this paper was communicated the nickel lines have been detected when a stream of nickel carbonyl ions keep running through the tube and the discharge is kept on for a short time with long intervals between the separate discharges.

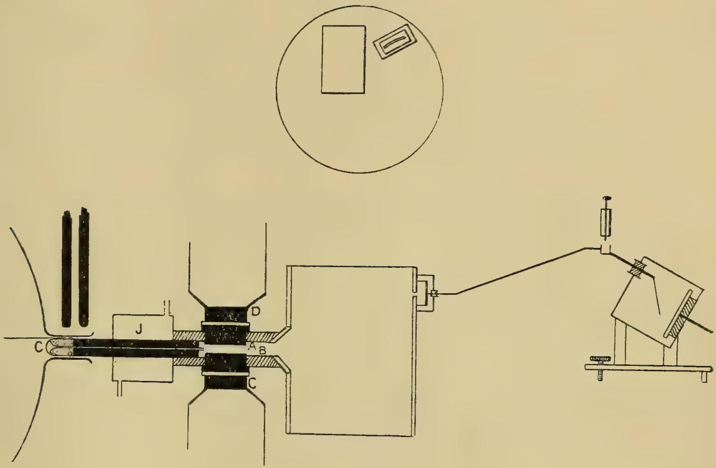
relative amounts, I have supplemented it by another method which enables us to measure the number of charged particles of any particular kind. The arrangement used for this purpose is represented in fig. 22. The particles, after passing through the electric and magnetic fields, fall upon the end of a closed cylindrical box, B. In the end of this box nearest the discharge-tube a parabolic slit 1 mm. in width is cut, the vertex of the parabola being the point where the undeflected rays would strike the end of the box, and the tangent to the vertex the line along which the particles would be deflected by the magnetic force alone. This slit is the only entry into the box. Thus all the particles which enter the box have the same value of e/m, and by altering the value of the magnetic field, one set of particles after another may be driven on to the slit and thus admitted into the box. Inside the box, and immediately behind the slit, there is an insulated long and narrow metal vessel placed so that every particle passing through the slit has to fall into this vessel. This vessel is connected with a Wilson tilted electroscope, so that the charge received by it can be measured.

At first considerable trouble was caused by the corpuscles which the metal around the slit emitted when it was struck by the positive rays ; to prevent these entering the Faraday vessel a permanent magnet was placed so as to produce a strong field between the slit and the Faraday vessel. This deflected the corpuscles away from the vessel without having any appreciable influence on the positive rays. A part of the front face of the vessel in which the Faraday cylinder was enclosed was cut away and a willemite screen inserted; by deflecting the positive rays on to this screen and observing the brightness of the parabolas, one could ascertain whether the conditions of the discharge-tube were such as to ensure a plentiful supply of positive rays. The face of the vessel, with the parabolic slit and phosphorescent screen, is represented in fig. 22.

The pressure in the observation tube was made as small as possible by the use of charcoal and liquid air ; the pressure in the part of the tube through which the discharge passed was generally about 3/1000 of a millimetre.

The Wilson electroscope gave a deflexion of about 100 divisions for a volt. The method of observation was as follows:—the positive rays were deflected by a constant electric field, and then the magnetic field was increased by small increments, and the deflexion of the Wilson electroscope in 10 seconds observed. Unless a parabola came on the slit there was practically no deflexion of the electroscope; as soon, however, as the magnetic force was such that a parabola came on the slit, there was a considerable deflexion, which vanished when the magnetic force was slightly increased so as to drive the parabola off the slit. The appearance and disappearance of the deflexion of the electroscope were surprisingly sharp, so that lines quite near each other could be detected and separated. With the first apparatus we tried, the power of separating the lines was not much inferior to the photographic method; and I believe that it is possible to improve the method by diminishing the width of the slit and making other improvements suggested by experience until it is more sensitive than the photographic method. It is in many ways more convenient as the tube has not to be continually opened to insert and remove the plates, it is more expeditious, and has the great advantage of being metrical. An example of the results obtained by this method is graphically represented in fig. 23. The abscissæ represent the magnetic force, the ordinates the deflexion of the electroscope in 10 seconds.

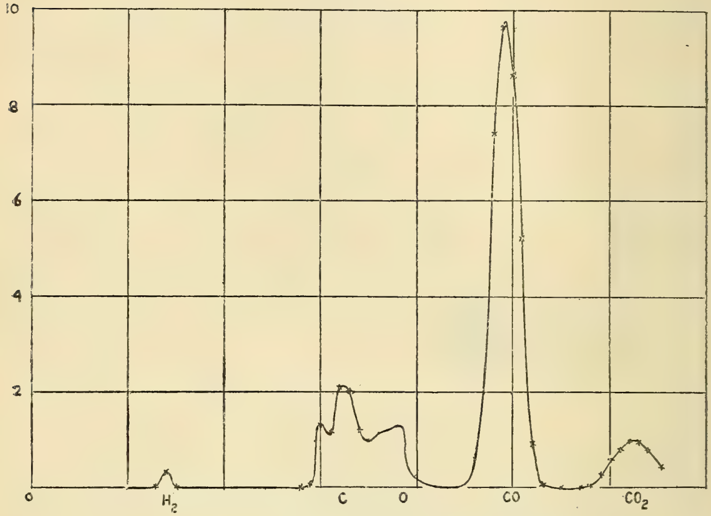
Fig. 22.



The gas in this case was carbon monoxide at a pressure of about 3/1000 of a millimetre. The nature of the particles producing the various peaks on the curve is indicated on the figure.

A comparison of this curve with a photograph of the discharge through the residual gas shows many interesting differences. On the photograph the strongest lines are those due to the hydrogen atom and molecule. The curve shows, on the other hand, that the number of hydrogen particles is only a small fraction of the number of CO particles. The extraordinary sensitiveness of the photographic plate for the hydrogen atom, in comparison with its sensitiveness to other atoms and molecules, is well brought out by this curve.

Fig. 23.



Carbon Monoxide, 320 Volts.

Another instance of the same effect is that when the discharge-tube is filled with mixtures of hydrogen and oxygen, the proportions of gases in the mixture may be altered within wide limits without producing any sensible effect on the relative brightness of the hydrogen and oxygen lines on the photograph. With the Faraday cylinder method, however, the magnitude of the effects found for the hydrogen and oxygen particles were roughly proportional to the amounts of these gases in the mixture. Examples for mixtures when the proportions by volume of the mixture were (1) 1 of H and 2 of O, and (2) 2 of H and 1 of O, are shown in figs. 24 and 25.

It will be noticed that in the mixture of hydrogen with two parts of oxygen, the number of charged oxygen molecules is greater than the number of charged atoms; while in the case of the mixture of two volumes of hydrogen to one of oxygen, the number of charged oxygen atoms appears to be greater than the number of charged oxygen molecules. This may possibly be due to a part of the peak ascribed to the oxygen atom being in reality due to molecules of water-vapour, the slit being hardly fine enough to separate values of m/e as close together as 16 and 18.

Fig. 24.

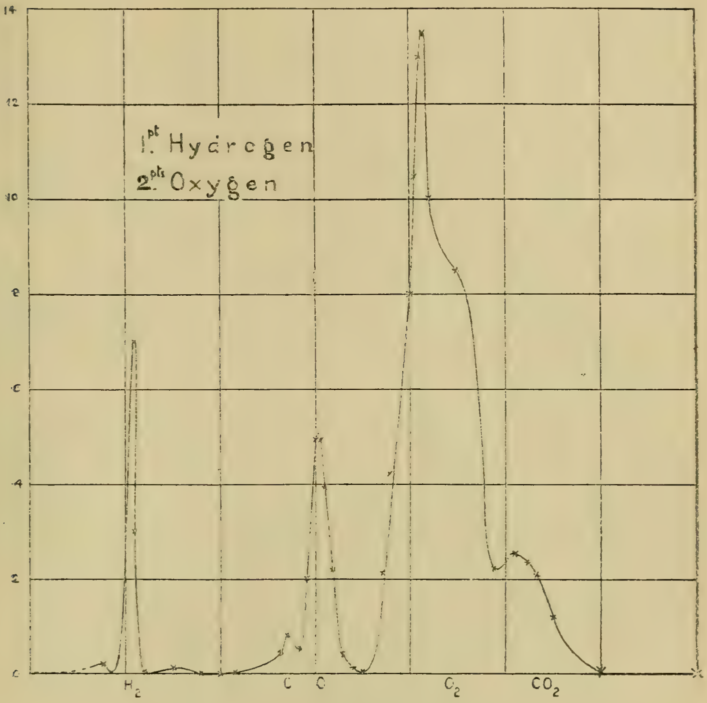
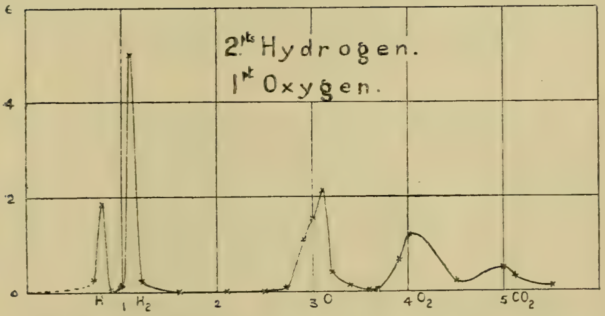


Fig. 25.



The negatively-charged hydrogen atoms seem to have the same preponderance in their effect on the photographic plate over other negative atoms as positive hydrogen has over other positive atoms. Thus on all the plates the line corresponding to the negative hydrogen atom is well marked, often comparable with the line due to the negative oxygen atom. With the Faraday cylinder method, the negative hydrogen atoms can only just be detected, while the negative oxygen ones produce large deflexions.

The discrepancy between the effects produced by hydrogen atoms and an equal number of heavy atoms is even more marked with a willemite screen than with a photographic plate: thus the willemite screen may show the hydrogen lines intensely bright, while the CO line is hardly visible, when measurements made with the Faraday cylinder show that the number of hydrogen particles is only a few per cent. of the number of CO particles. An interesting point and one that requires further investigation, is that with the heaviest particles of all, the mercury ones, the discrepancy between the results obtained with the Faraday cylinder and the photographic plate is not so great as it is with some of the lighter particles.

When the positive rays are detected by a phosphorescent screen or a photographic plate, we find that whatever gas may be in the discharge-tube, the hydrogen lines are strong; this suggests that in all gases there are a great number of positive carriers having the same mass as the atom of hydrogen. With the Faraday cylinder method, however, we find that the number of charged atoms of hydrogen is small unless hydrogen is introduced into the tube; this small quantity is not greater than that which might be accounted for by gas given out by the electrodes or liberated from the walls of the discharge-tube. The results obtained with the screen and plate are thus due to the abnormal sensitiveness of these agents to the rapidly moving hydrogen atoms, which makes them give a false estimate of the number of these atoms taking part in the discharge.

Are the atoms in the molecule of a gas charged one with positive the other with negative electricity?—It is a matter of fundamental importance to know if the atoms in the molecules of gases, compound or elementary, are charged with electricity or not. In a molecule of hydrogen, for example, is one atom positively, the other negatively, charged? In a molecule of hydrochloric acid gas, is the hydrogen positively, the chlorine negatively, charged? In a molecule of ammonia, has the nitrogen atom three negative charges and each of the hydrogen atoms one positive charge? It seems to me that we can get valuable information on this point by the study of the positive rays, now that, by the Faraday cylinder method, we can measure the number of positive rays of any kind taking part in the discharge. Let us take as an example the case of CO. If the carbon atom in this compound were positively charged, the oxygen atom negatively, then if a molecule of CO were split into atoms by the impact of a positive particle, the carbon atom would be positively electrified, the oxygen one negatively. The negatively electrified oxygen atom would move away from the cathode, and though it might after reaching the negative glow sometimes acquire a positive charge and be attracted to the cathode and become a positive ray, we should expect that the number doing so would be small compared with the number of carbon atoms which start with a positive charge. Thus, if the atoms in CO are charged we should expect to find in the positive rays produced when the discharge passes through CO, a much greater number of carbon atoms than of oxygen ones. I have investigated by the Faraday cylinder method the discharge through CO, the result is represented in fig. 23. It will be seen that the number of positively charged carbon atoms only exceeds that of the positively charged oxygen ones in the ratio of 11 to 7; and this number underestimates the number of oxygen atoms which came through the cathode, for some of these after getting through the cathode acquired a negative charge. Measurements by the Faraday cylinder showed that about 2/7 did so, while the number of carbon atoms acquiring a negative charge was insignificant in comparison. Taking the negative oxygen atoms into account as well as the positive, we find the proportion between the carbon atoms and the oxygen ones as 11 to 9; the numbers are so nearly equal as to preclude the atoms carrying opposite electrical charges when in the molecule.

Further evidence against the existence of these charges on the atoms is afforded by the consideration of the number of atoms in the positive rays which carry multiple charges. If the atoms in CH_4 or CO_2, for example, were charged, we should expect to find a considerable number of carbon atoms with four charges, whereas as a matter of fact no such atoms have been observed.

The view of the forces between the atoms in the molecule of a gas which is most in accordance with the behaviour of the positive rays, is that these forces are due to the atoms behaving somewhat after the manner of electrical doublets;

i. e., that the total charge on each atom forming a part of a gaseous molecule is zero, but that in each atom the positive and negative charges are so arranged that the force between adjacent atoms is attractive. I have not yet, however, tried any compound which is a strong electrolyte, it is possible that the atoms in such a compound might be charged.

There is, I think, other evidence besides that derived from positive rays in favour of the view that the atoms as a rule are not charged. For example, dissociation of gases at quite low temperatures (say 70° C.), such as takes place with nickel carbonyl, is not accompanied by any abnormal conductivity. And although, as I showed many years ago (Phil. Mag. [5] xxix. pp. 358–441), there is considerable conductivity at high temperatures in gases which dissociate at these temperatures, yet this conductivity seems to depend greatly on the contact of these gases with the hot metal of the electrodes between which the current is measured; suggesting that the charging up of the atoms in this case may be due to the electricity which we know to be emitted by hot metals. Quite recently Schmidt (*Ann. d. Phys.* xxxv. p. 401) has observed considerable conductivity at temperatures less than 200° C. in a vessel containing the vapour of cadmium iodide, obtained by heating the salt in the vessel in which the conductivity is observed. The cadmium iodide is dissociated, but we do not know whether the conductivity is due to cadmium iodide which has existed as vapour and then been dissociated, or whether it is due to systems which were dissociated when driven off from the salt by the heating. In the second case other considerations would come in, which can be illustrated by considering the case of electrolytes in solution, when the dissociation of the salt seems to be accompanied by the charging up of the atoms. If the atoms get charged in the electrolyte, it may be asked, why should they not get charged in the case of gases? The conditions are very dissimilar. We may regard the two atoms in the molecule as analogous to the two plates of a condenser, and the acquisition of a charge by the atoms as analogous to the charging up of the condenser. Now the work required to give a fixed charge to a condenser is inversely proportional to the capacity of the condenser, so that the smaller the capacity the greater is the amount of energy required to charge it. We should, however, expect that the capacity of a molecule when in the gaseous state would be much less than when it was in solution in a liquid of large specific inductive capacity; the specific inductive capacity would of itself increase the capacity, and in addition there would be the opportunity of the atoms in the molecule forming aggregates, thus becoming, from this point of view, much larger systems and having greatly increased capacity. The same considerations would apply to a gas forming a surface layer on a piece of metal or on a solid or liquid, and may account for the electrification observed when gases bubble through liquids.

In the case of salts in flames when there is also ionization, it is to be remarked that the ionization is not of the type that would be produced if the metal in the salt were positively electrified and the acid radicle negatively; for in this case the carriers of the negative electrification are corpuscles and not negatively electrified atoms. The charging up of the positive ion in the flame may be analogous to the emission of negative corpuscles from hot metals.

L. Bloch (*Annales de Chimie et de Physique*, xxii. pp. 370 & 441, xxiii. p. 28), who has made a very interesting series of experiments on the connexion between chemical charge and ionization, found that the flame of burning sulphur did not conduct when its temperature was below 400° C., but had great conductivity when the temperature was raised to a much higher value. He further showed that in the many cases of chemical action on which he made observation, which included the dissociation of arseniuretted hydrogen, the oxidation of nitrogen bioxide, the action of chlorine on arsenic, the chemical action was not accompanied by ionization.

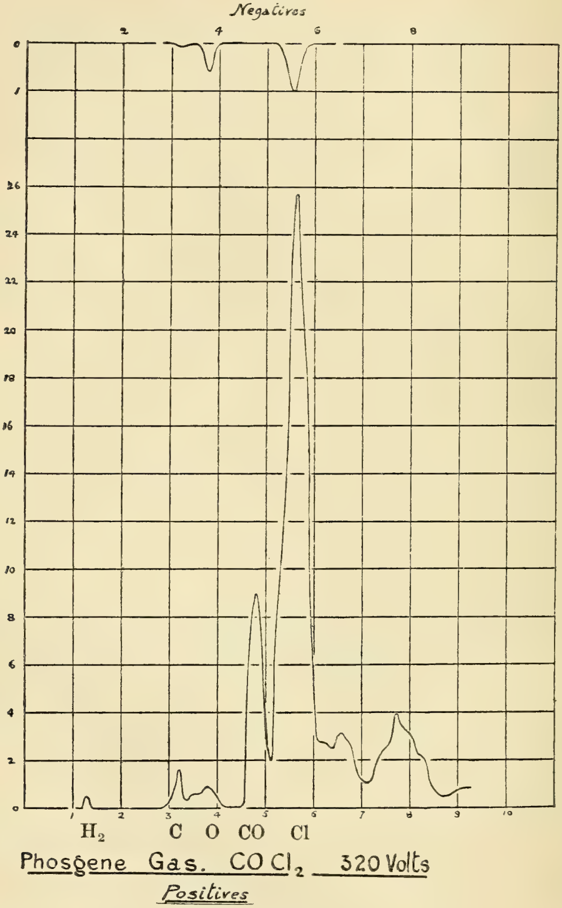
The Faraday cylinder method may be used to obtain information as to how the various atoms in a complicated molecule are linked together.

A curve got by the use of the Faraday cylinder method when the discharge passed through phosgene gas $COCl_2$, is shown in fig. 26. The curve shows that the carriers of the positive electricity were the atoms of C, O, Cl, the molecule of CO, Cl_2 and CCl and $COCl_2$; the negative carriers were C, O, Cl. It will be noticed that only a small fraction of the current is carried by free carbon and oxygen atoms, showing that in phosgene the carbon and oxygen atoms are so firmly united that the greater part of them remain combined even when the gas is dissociated. Fig. 27 is the curve for CO_2.

Retrograde Rays.

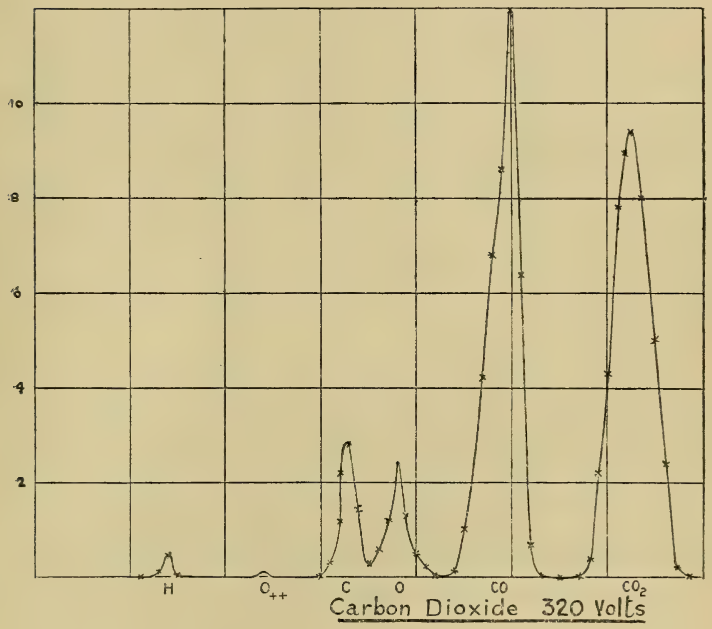
The existence of positively electrified particles moving away from the cathode was observed by Villard (*Comptes Rendus*, cix. p. 42) and the author. I have recently succeeded in obtaining a photograph of these rays. The method employed was to use the perforated electrode which in the previous experiments had served as the cathode for the anode, and to use for the cathode a flat plate of aluminium placed so that the normal to its plane passed through the hole in the other electrode. By giving an exposure of over an hour and using a larger tube (about 1 mm. in diameter) for the perforated electrode, I have

Fig. 26.



succeeded in getting photographs of these rays, one of which is reproduced in fig. 28 (Pl. IX.); the definition is not good owing to the size of the tube. But in the photograph can be seen rays corresponding to the hydrogen atom and molecule and to the oxygen atom. An interesting point about the photograph is that the negative side (the left) is stronger than the positive, and shows negatively electrified hydrogen atoms and molecules and oxygen atoms. Thus, in addition to the cathode rays and positively electrified retrograde rays, we have streaming from the cathode negatively electrified atoms and molecules; the photograph shows that the maximum velocity of the negative atom is about the same as that of the corresponding positive one. This, I think, confirms the view I expressed in a former paper that these positive retrograde rays are atoms or molecules which get negatively electrified near the cathode, are then repelled from it by the electric field, and subsequently, by collision, lose a negative charge and acquire a positive one. The photographs show, since the negative side is stronger than the positive, that in this case the majority of the charged atoms had retained their negative charge.

Fig. 27.



I wish to record my indebtedness to Mr. F. W. Aston, B.A., whose skill in designing and making the numerous pieces of apparatus required in these investigations has been of the greatest assistance, and also to Mr. E. Everett.

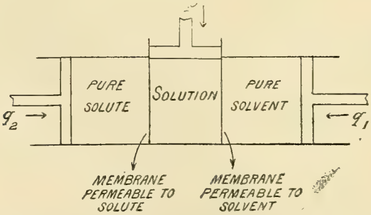
XX. *Solubility and Supersolubility from the Osmotic Standpoint.* *By the* Earl of BERKELEY, *F.R.S.*[*]

(1) HITHERTO solubilities and supersolubilities have been discussed from the point of view of phase rule solubility curves. I propose here to indicate another method, that of osmotic equilibria, which seems to throw additional light on the subject; and at the same time I will outline a hypothetical explanation of some of the observed phenomena.

(2) I will preface my remarks by drawing attention to the fact that every binary mixture has, at a given temperature, two osmotic pressures, one which is realizable by means of a membrane permeable to the solvent, and the other, which will be called the "conjugate" osmotic pressure, realizable by a membrane permeable to the solute. Over and above these, there are an infinite number of osmotic pressures which merely depend on the standard conditions of pressure adopted: thus, there is one set definable by the condition that the pressure on the solvent remains constant, and another set definable by the condition that the pressure on the solution remains constant; and further, both these sets give different osmotic pressures according to the magnitude of the constant pressure.

(3) Unless otherwise stated, the temperature will be assumed constant, and the phrase "osmotic pressure" will refer to solutions under a constant pressure p; it will mean the algebraic difference of pressure between p and the pressure q (whether positive or negative) which has to be put on the solvent to keep it in osmotic equilibrium with the solution; similarly with the conjugate osmotic pressure. The conditions required are realized in fig. 1, where the osmotic pressure is the difference between p and q_1, while the conjugate is that between p and q_2; the osmotic pressures for all concentrations being measured with the same pressure p on the solutions.

Fig. 1.



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[*] Communicated by the Author.

(4) Before proceeding to the discussion of the osmotic pressure-concentration curves, I will establish two propositions which, indeed, are almost self-evident.

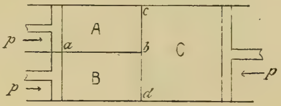
It is impossible that osmotic equilibrium can exist when the rate of change of osmotic pressure with concentration is negative.

Consider a beaker containing a mass of solution; if it were possible for the osmotic pressure to decrease with an increase of concentration, then, no solution being perfectly homogeneous, assume that momentarily at the point A we have an increase of concentration. Diffusion, being a direct function of osmotic pressure, will cause the concentration of one of the components at A to go on increasing until the whole of it is concentrated there; which is absurd!

(5) *Two solutions which are in osmotic equilibrium with a third solution are in equilibrium with one another* *.

Consider the system shown in fig. 2, where A and B are the two solutions in equilibrium with solution C—all three being under the same pressure p, and ab and cd being membranes permeable to the common solvent.

Fig. 2.



Assume that the osmotic pressure of A is greater than that of B, then (the necessary manipulation of shutters closing the membranes being understood) solvent will flow into A from B, but the concentration in B will thereby be increased and will cause a flow of solvent into it from C, which in its turn takes solvent from A, thus setting up perpetual motion. A and B have therefore the same osmotic pressure, and C can be replaced by the pure solvent under a suitable pressure without disturbing the equilibrium.

(6) The following thermodynamic relations must also be established; they were worked out at my suggestion by Dr. C. V. Burton. The proof here given, though more lengthy than that based on the thermodynamic potential, will no doubt be more readily followed by physical chemists.

Let P_1 and P_2 be the ordinary and conjugate osmotic pressures respectively.
c_1 ,, c_2 be the number of grammes of solvent and solute respectively in one gramme of solution.
s_1 ,, s_2 be the spaces occupied in the solution by one gramme of solvent and of solute respectively.

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* This can be derived from the "Law of the Mutuality of Phases"—see Nernst, 'Theor. Chemistry,' 3rd English edition, p. 662.

Let q_1 ,, q_2 be the pressures on the solvent and solute respectively when they are in osmotic equilibrium with the solution.

u_1 ,, u_2 be the specific volumes of the solvent and solute when under pressures q_1 and q_2 respectively.

σ_1 ,, σ_2 be the specific volumes of the solvent and solute crystals respectively, when under pressure p.

w be the specific volume of the solution when under pressure p.

$\partial P/\partial c$ refer to the solutions when under constant pressure.

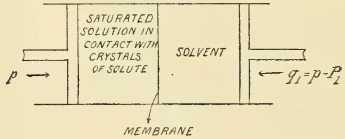
$\mathfrak{d}P_1/\mathfrak{d}c_2$ and $\mathfrak{d}P_2/\mathfrak{d}c_1$ refer to the solutions when the solvent and solute respectively are under constant pressures.

dc_1/dp and dc_2/dp be the pressure coefficients of solubility of the solvent and solute respectively.

This notation, unless otherwise stated, will be followed throughout the communication.

Perform a reversible isothermal cycle on the system shown in fig. 3. As all terms in the final summation, other than those in $m\delta p$, cancel out, it will only be necessary to consider the latter.

Fig. 3.



1*st Operation.*—Keeping the pressures constant, push a mass m of the solvent from left to right in the figure. This operation contributes no term in $m\delta p$.

2*nd Operation.*—Without transference through the membrane, increase the pressure on the left to $p+\delta p$, and on the right to

$$p-P_1+(1-\partial P_1/\partial p-\partial P_1/\partial c_2 \,.\, dc_2/dp)\delta p.$$

The work term on the left is

$$-pm\delta p\left[-\frac{1}{c_1}\left(\frac{\partial w}{\partial p}+\frac{\partial w}{\partial c_2}\frac{dc_2}{dp}\right)-\frac{w}{c_1{}^2}\frac{dc_2}{dp}+\frac{c_2}{c_1}\frac{d\sigma_2}{dp}+\frac{\sigma_2}{c_1{}^2}\frac{dc_2}{dp}\right],$$

and that on the right is

$$-(p-P_1)(1-\partial P_1/\partial p-\partial P_1/\partial c_2 \,.\, dc_2/dp)du_1/dq_1 \,.\, m\delta p.$$

3rd Operation.—Keeping both pressures constant, drive back mass m of solvent from right to left. The work term on the left is

$$-m\delta p\left(\frac{w}{c_1}-\frac{c_2}{c_1}\sigma_2\right)-pm\delta p\left[\frac{1}{c_1}\left(\frac{\partial w}{\partial p}+\frac{\partial w}{\partial c_2}\frac{dc_2}{dp}+w\frac{dc_2}{dp}\right)-\frac{c_2}{c_1}\left(\frac{\sigma_2}{c_1c_2}\frac{dc_2}{dp}+\frac{d\sigma_2}{dp}\right)\right],$$

and that on the right is

$$(p-\mathrm{P}_1)m\delta p\frac{du_1}{dq_1}\left(1-\frac{\partial \mathrm{P}_1}{\partial p}-\frac{\partial \mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right)+m\delta p\left(1-\frac{\partial \mathrm{P}_1}{\partial p}-\frac{\partial \mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right)u_1.$$

4th Operation.—Without transference through the membrane, reduce the pressures to their original values. This operation contributes no terms in $m\delta p$.

Equating the work done by the external forces to zero, we get

$$\frac{w}{c_1}-\frac{c_2}{c_1}\sigma_2=u_1\left(1-\frac{\partial \mathrm{P}_1}{\partial p}-\frac{\partial \mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right).$$

Remembering that

$$\partial \mathrm{P}_1/\partial p=(u_1-s_1)/u_1 \quad \text{and} \quad \partial \mathrm{P}_1/\partial c_2=s_1/u_1\,.\,\frac{\boldsymbol{\partial}\mathrm{P}_1}{\boldsymbol{\partial}c_2},$$

this reduces to

$$\frac{dc_2}{dp}=\frac{c_2(\sigma_2-s_2)}{c_1s_1\boldsymbol{\partial}\mathrm{P}_1/\boldsymbol{\partial}c_2}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

A similar result for the conjugate osmotic pressures and crystals of the solvent is obtained by performing the same cycle on a system under suitable imaginary conditions.

(7) In this connexion it may not be out of place to point out that an exact relation, giving the change of solubility with temperature when the pressure on the solution is constant, may be obtained; Cohen *, quoting Braun †, gives the following thermodynamical relation between the pressure and temperature coefficients of solubility—

$$\frac{dc_2}{dt}\bigg/\frac{dc_2}{dp}=\frac{\mathrm{L}}{(\sigma_2-s_2)t},$$

where t is the temperature and L the heat of solution.

Substituting (1) in this expression, we get

$$\frac{dc_2}{dt}=\frac{c_2\mathrm{L}}{c_1u_1t\partial \mathrm{P}_1/\partial c_2}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(8) A corresponding cycle can be applied to partially miscible liquids. Before doing so, it is necessary to show

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* *Zeit. Phys. Chem.* vol. lxxv. p. 262.

† *Zeit. Phys. Chem.* vol. i. p. 261.

that any two liquid phases which are in equilibrium with one another have the same osmotic pressure.

Referring to fig. 2, let A represent the solute saturated with solvent (this will be called the 2nd phase), and B the solvent saturated with solute (the 1st phase), and *ab* the surface of separation. A and B are in equilibrium with one another, and this equilibrium will not be disturbed if *ab* represents a membrane permeable to the solvent. If C represents a solution in osmotic equilibrium with B, it is easy to show, by a similar process to that outlined in paragraph (5), that A will also have the same osmotic pressure as C, so that C can be replaced by the solvent under pressure q_1 *.

(9) On this system as now defined, perform the same cycle as in paragraph (6) and designate the new quantities involved thus :—

c_1' and c_2' are the number of grammes of solvent and solute respectively in one gramme of the second phase.

s_1' and s_2' are the spaces occupied, in the second phase, by one gramme of solvent and of solute respectively.

x is the specific volume of the second phase.

As before, we need only consider the terms in $m\delta p$, and the 1st and 4th operations do not contribute any terms to the final result. In the 2nd operation the work term on the left is

$$pm\delta p\left\{\frac{c_2'}{c_2'-c_2}\frac{dw}{dp}-\frac{c_2}{c_2'-c_2}\frac{dx}{dp}+\frac{x-w}{c_2'-c_2}\left[-\frac{c_2'}{c_2'-c_2}\frac{dc_2}{dp}+\frac{c_2}{c_2'-c_2}\frac{dc_2}{dp}\right]\right\},$$

and that on the right is

$$-(p-\mathrm{P}_1)m\delta p\frac{du_1}{dq_1}\left[1-\frac{\partial\mathrm{P}_1}{\partial p}-\frac{\partial\mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right].$$

In the third operation the work term on the left is

$$-\frac{m\delta p}{c_2'-c_2}\left\{c_2'w-c_2x+p\left[\frac{dc_2'}{dp}\left(\frac{-c_2'w+c_2x}{c_2'-c_2}+w\right)\right.\right.$$
$$\left.\left.+\frac{dc_2}{dp}\left(\frac{c_2'w-c_2x}{c_2'-c_2}-x\right)+\frac{c_2'dw}{dp}-\frac{c_2dx}{dp}\right]\right\},$$

---

* Incidentally attention may be drawn to the fact that by a similar process of reasoning it can be shown that if one liquid phase is in equilibrium with a solid component, the other phase must also be in equilibrium with it. Thus, two liquid phases in equilibrium with one another have the same freezing-point.

and on the right it is

$$(p-\mathrm{P}_1)m\delta p\frac{du_1}{dq_1}\left[1-\frac{\partial \mathrm{P}_1}{\partial p}-\frac{\partial \mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right]+\left[1-\frac{\partial \mathrm{P}_1}{\partial p}-\frac{\partial \mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right]u_1 m\delta p.$$

The total work done by external forces on the left is

$$-\frac{m\delta p}{c_2{}'-c_2}(c_2{}'w-c_2x),$$

and on the right it is

$$u\left[1-\frac{\partial \mathrm{P}_1}{\partial p}-\frac{\partial \mathrm{P}_1}{\partial c_2}\frac{dc_2}{dp}\right]m\delta \mathrm{P}_1.$$

Equating the sum of these to zero we get

$$\frac{dc_2}{dp}=\frac{c_2{}'w-c_2x-s_1c_2{}'+s_1c_2}{s_1(c_2{}'-c_2)\partial \mathrm{P}_1/\partial c_2}$$

or

$$\frac{dc_2{}'}{dp}=\frac{c_2{}'w-c_2x-s_1{}'c_2{}'+s_1{}'c_2}{s_1{}'(c_2{}'-c_2)\partial \mathrm{P}_1{}'/\partial c_2{}'}.$$

These, remembering that $w=c_1s_1+c_2s_2$ and that $x=c_1{}'s_1+c_2{}'s_2{}'$, reduce to

$$\frac{dc_2}{dp}=\frac{c_2c_1{}'(s_1-s_1{}')+c_2c_2{}'(s_2-s_2{}')}{(c_2{}'-c_2)s_1\partial \mathrm{P}_1/\partial c_2}$$

or

$$\frac{dc_2{}'}{dp}=\frac{c_2{}'c_1(s_1{}'-s_1)+c_2c_2{}'(s_2{}'-s_2)}{(c_2-c_2{}')s_1{}'\partial \mathrm{P}_1{}'/\partial c_2{}'} \quad . \quad . \quad . \quad (3)$$

(10) A corresponding relation to that given in equation (2) can be derived by putting $dp=0$ in Planck's equation, No. 170 *; we then get

$$\frac{dc_2}{dt}=-\frac{c_2(c_1{}'\mathrm{L}_1+c_2{}'\mathrm{L}_2)}{t(c_2{}'-c_2)s_1\partial \mathrm{P}_1/\partial c_2}, \quad . \quad . \quad . \quad . \quad (4)$$

where L_1 is the heat absorbed when unit mass of solvent passes from the first to the second phase, and L_2 is the heat absorbed when unit mass of solute passes from the first to the second phase.

(11) We are now in a position to deal with the osmotic pressure-concentration curves.

The most instructive case is that of two partially miscible liquids; and it may be mentioned that the main features of the graphs give the phenomena both for ionized and non-ionized liquids.

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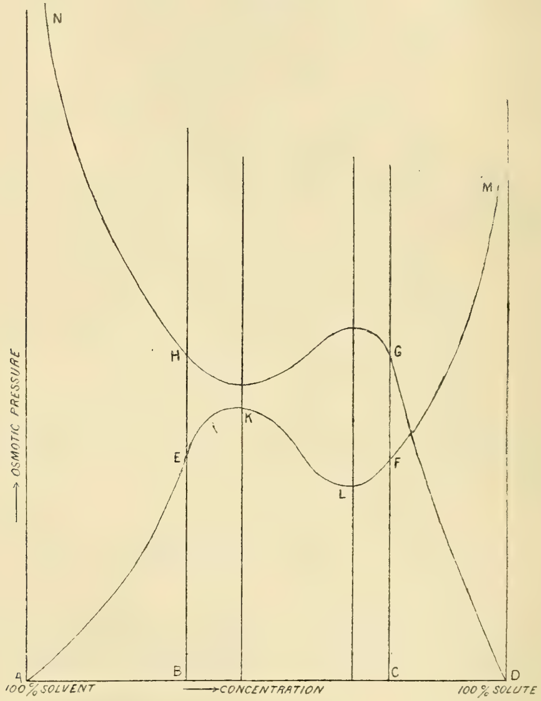
* Planck's Thermodynamics, Ogg's translation, p. 194.

The curves AE, FM, DG, and HN in fig. 4 represent the definite information that theory and such experiments as have been made give us.

Dealing with the ordinary osmotic pressure first; the curve starts from A as a straight line (Boyle's law) and passes upward concave to the ordinate through A (the curve is given this form because, hitherto, no cases of convexity have been observed) till it meets the ordinate through B, which represents the limit of solubility in that phase. It leaves the limit of solubility CF, in the other phase, at F,

Fig. 4.



where CF = BE (see paragraph (8)), and probably remaining concave upwards, it touches the ordinate through D at infinity.

(12) This last proposition is provable thus:—In this Magazine, series 6, vol. xvii. 1909, p. 604, Dr. Burton and I have established the following exact relations,

$$\frac{\mathfrak{d}P_1}{\mathfrak{d}c_2}=\frac{c_2 s_2}{c_1 s_1}\frac{\mathfrak{d}P_2}{\mathfrak{d}c_1} \quad \text{and} \quad \frac{\partial P_1}{\partial c_2}=\frac{s_1}{u_1}\frac{\mathfrak{d}P_1}{\mathfrak{d}c_2},$$

from which

$$\frac{\partial P_1}{\partial c_2} = \frac{c_2 u_2}{c_1 u_1} \frac{\partial P_2}{\partial c_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now the conjugate osmotic pressure-curve starts from D as a straight line (Boyle's law), hence $\partial P_2/\partial c_1 = \text{a constant} = k$;

$$\therefore \quad \frac{\partial P_1}{\partial c_2} = \frac{c_2 u_2}{c_1 u_1} k.$$

On integrating this expression and remembering that c_1 is vanishingly small, it follows that P_1 must at the limit contain an infinite logarithm and must therefore be infinite.

The conjugate osmotic pressure-curve is essentially similar, and cuts the ordinate through C at some point which we cannot specify, say at G, it then leaves BE at H, where BH = CG, and approaches the ordinate through A asymptotically.

(13) If we take some other constant temperature we shall obtain another pair of curves in which the position of the points E, F, G, and H will be different. Similarly if we take some other constant pressure on the solutions. And, in general, given the pressure (or temperature), E and F will coincide at a definite temperature (or pressure) (G and H will coincide simultaneously on the same ordinate), this point being the critical osmotic pressure and concentration for the particular pressure (or temperature) concerned; that is, the point where the two liquids become miscible in all proportions. The locus of the points E and F will be the "border curve" for the ordinary osmotic pressure, while the locus of G and H is the border curve for the conjugate.

(14) If we were to plot the curves for osmotic pressures defined by the condition that the pressure on the solvent and the solute respectively were constant, in general, the principal modification would be that, for the conjugate, neither of the points of limited solubility would be on the same ordinates as those of the ordinary osmotic pressure.

(15) We will now discuss the inferences which may be drawn from the curves.

Dealing first with the paths between E and F, and G and H; all experience with single-phase systems shows that their properties are throughout continuous—we may therefore safely postulate that E and F (and G and H) must be joined in a smooth manner—and, as BE = CF, the only way to do this is to carry on the curve AE upwards and MF downwards, and join them by a curve containing at least two points where $\partial P_1/\partial c_2 = 0$, say at K and L. From equation (5), when

$\partial P_1/\partial c_2 = 0$, we have also $\partial P_2/\partial c_1 = 0$, hence the horizontal tangents to the conjugate have their points of contact on the same ordinates as K and L. The fact that we have to prolong the curves through the limits of solubility shows that supersolubility is always theoretically possible; and I would suggest that the ordinates through the points of contact of the horizontal tangents represent the absolute limit of supersaturation, for after these ordinates are passed $\partial P_1/\partial c_2$ is negative, and by paragraph (4) instability *must* set in *.

(16) Referring to the mechanism by which a liquid mixture separates into two liquid phases. There are three possible ways of bringing this about, and, in all three, changes in osmotic pressure are involved.

(*a*) By changing the temperature of the liquid. In all cases examined the first appearance of the new phase is heralded by a cloudiness throughout the liquid. This cloud is supposed to be due to minute globules of the new phase †.

(*b*) By altering the pressure on the liquid. I am not aware of any record dealing with the first appearance of the new phase under these conditions. Doubtless a cloudiness is also apparent.

(*c*) By altering the concentration. This method is analogous to evaporating off one of the components at constant temperature; and it is realizable in the system shown in fig. 5 by decreasing the pressure q_1 and thus causing solvent to flow from left to right. Here again no experimental evidence of the formation of globules is available, but judging by the evaporation analogy we are justified in assuming that they would appear.

We will discuss method (*c*) as it has the advantage, so far as our diagram is concerned, of involving no change in the temperature and pressure of the solutions.

If we leave out of account what may be called the accidental setting in of instability, the globules, on the hypothesis postulated in paragraph (15), will appear only when the mixture has reached the point K. Probably they can only be visible when the separate entities have acquired the property of surface tension ; the circumstances determining this are not yet ascertained, but we can assert with considerable plausibility, that a separating surface is not possible until the number of molecules contained in the incipient globule is large.

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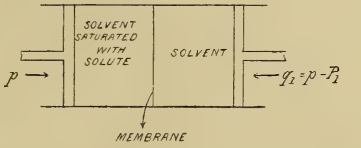
* Instability may set in before these points are reached; for, apart from the presence of "nuclei," there may be intermolecular forces whose effect we are unable to forecast.

† See Donnan, Chem. News, vol. xx. p. 139 (1904); Rothmund, *Zeit. Phys. Chem.* vol. lxiii. p. 76 (1908); von Lepkowski, *Zeit. Phys. Chem.* vol. lxxv. p. 608.

Fig. 5.



(17) It is necessary to consider the question of the concentration inside the globules at some length—for, although we are about to deal with unstable conditions, yet some light may be thrown on the cause of the difference between solutions of solids in liquids and solutions of imperfectly miscible liquids. It might be thought that as a solution is only a collection of two sets of molecules, these in virtue of their mobilities will, given time enough, have all possible relative concentrations at some point or other in the mass, and the separation into two phases occurs when the concentration has reached, at one of these points, a value represented by the ordinate through F of fig. 4. It can readily be shown that this explanation cannot be a general one ; for take the case of benzene and water, whose mutual solubility is very small, and suppose we have a litre of a homogeneous saturated solution of benzene in water, and calculate, on ordinary probability data (preferential molecular attractions are excluded), the time it would require for the concentration at any point in the mass to be that at F (*i.e.* one molecule of water to 6000 molecules of benzene), we shall find that 10^{11000} years would have to elapse before this state were reached !

A more plausible hypothesis is the following : assume that at some point or other in the mixture, which is about to separate, a few molecules of the pure solute come together by hazard (on probability data this is quite possible) and that these have a preferential attraction for their own species ; it is easy to see that growth would continue until separation ensued. The main objection to this explanation is that diffusion (a direct function, in this case, of a nearly infinite osmotic pressure ; point M of figure) must be acting all the time against the further growth of the aggregate *.

* This hypothesis may be strengthened by assuming that the preferential attraction of the pure solute molecules ceases when a certain limit is reached, the aggregate then taking in, by diffusion, solvent molecules ation required by point F of diagram.

(18) I would suggest the following explanation as involving the least assumptions. No solution is truly homogeneous, consequently, in a liquid at the limit of supersaturation, a small departure from the mean concentration in the direction of the other phase will surely take place. This new aggregate of molecules, having $\partial P_1/\partial c_2$ or $\partial P_2/\partial c_1$ negative as the case may be, will, by paragraph (4), go on increasing in concentration until a new state of equilibrium is reached. This aggregate, or incipient globule as we may call it, will itself be unstable and will tend to throw out the other phase, thus contributing to the separation into two phases. The conditions being unstable it is impossible to follow the events taking place in the globule, the more so as when the property of surface tension is acquired there will be pressure* and small concomitant temperature changes † involved. But, although at first sight equilibrium should be reached instantaneously, yet, as the supply of molecules for further growth can only be obtained through the relatively slow process of diffusion, we can state that a finite time will be required before the final concentration is reached.

During this interval ot time the globules will *tend* to one or the other of the two final states of equilibrium which are represented by equations (1) and (3) respectively. In the first case the separating phase is a pure solid, in the second it is a liquid mixture.

(19) An example will show this more clearly : suppose we have a saturated solution of water in ether, under constant pressure as in fig. 5, with the solvent, pure ether, in the right-hand compartment. Assume the temperature such that on the withdrawal of a small quantity of the ether, ice is formed —equation (1) has been operative on the contents of the globules. If, however, the temperature had been very slightly higher, the liquid phase, water saturated with ether, would have come out, and in that case equation (3) was operative. It is evident, had we assumed an unsaturated solution of water in ether to start with, the withdrawal of ether, at the right temperature, could only lead to the formation of ice. Here again I would suggest that the first change which takes place is the formation of globules richer in ether, which having $\partial P/\partial c$ negative are unstable, and tend, under the influence of their own internal pressure, to the only equilibrium possible, namely that represented by equation (1).

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* A droplet of water of ·0005 cm. diameter has an internal pressure, due to surface forces, of 6·4 atmos : it still contains 10^8 molecules.

† Owing to the small size of the globules these temperature changes will be negligibly small.

(20) The foregoing discussion indicates how the properties of a binary liquid solution depend on the temperature and pressure under which it is observed. If we exclude irreversible chemical changes and metastable states, we may accordingly place any solution in one of the following categories :—

State 1.—If the temperature and pressure are such that no alteration in the concentration of the solution will cause it to throw out another phase, it is in State 1, and the components are completely miscible. This state is characterized by the solutions having $\partial P/\partial c$ positive throughout the whole range from $c=0$ to $c=1$.

State 2.—If the temperature and pressure are such that the only phase which comes out when the concentration is altered is a liquid or gaseous one, then the solution is in State 2, and the components are partially miscible[*]. It is characterized by the fact that on throwing out the liquid or the gaseous phase, equation (3) has been operative on the globules.

State 3.—If the temperature and pressure are such that an alteration of the concentration in one direction or the other (or both) causes a solid phase to come out, the solution is in State 3. This state includes, at ordinary temperatures and pressures, most solutions of solids in liquids, and is characterized by the operation of equation (1) on the contents of the globules.

This category embraces all cases where an alteration in the concentration in one direction causes the appearance of a solid, while in the other direction a liquid phase, or even a gaseous phase, may be thrown out.

(21) It follows from the above that (assuming no irreversible change takes place), as the solubility of sugar in water increases both with rise of temperature and increase of pressure, we should get a solution of these two substances in State 1—probably somewhere above the melting-point of sugar—and presumably at some slightly lower temperature we could obtain partially miscible liquids, where liquid sugar saturated with water would be thrown out. It must not be forgotten that as there is a limit to the negative pressure[†] which a solution (or, for that matter, a pure liquid) will support, there may be cases (*e. g.* those in which the solubility decreases with increase of pressure) where the three states above enumerated may not all be realizable.

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[*] In a solution of a gas in a liquid, as there is partial solution, the components come under this designation.

[†] If the solution were able to support an infinite negative pressure (apart from a defect of adhesion to the containing walls), it would imply an infinite attraction between the molecules, which is scarcely possible.

(22) The evidence for the existence of a limit to the supersaturation of a solution seems to be strengthened by the following.

Numerous investigators * have shown that supersaturated solutions can be made to crystallize out by mechanical shock. Thus, Mr. Applebey, working in my laboratory in the usual way with sealed glass tubes containing the solution, together with a short length of brass rod, has obtained results with supersaturated sugar solutions which show that the faster the tubes are shaken, the higher the temperature at which crystallization takes place—the maximum speed he was able to use was 700 up and down strokes per minute, and the freedom of path of the 1·5 inch length of No. 5 B.A. brass rod was about one inch.

(23) I have lately made some experiments similar to those described by Young †. Various forms of apparatus were devised and tried; the most successful of these is shown in fig. 6.

The glass tube A (one inch internal diameter), containing the solution, is rigidly held in the water bath, which is furnished with a thermostat and stirrer (not shown). The steel anvil B, whose upper surface has been rendered as hard as possible by quenching in a freezing-mixture, passes through the indiarubber stopper closing the lower end of A. A brass tube C, passed through the upper indiarubber stopper, acts as a guide for the steel rod D, whose lower end is ground hemispherical and also hardened; this rod is normally held about 0·5 mm. from the surface of B by means of the thin rubber tubing E, but it is brought into violent contact with the anvil when the spring F is released. The mechanism actuating the spring explains itself.

It was found that some forty blows, each developing a pressure of approximately 20,000 atmospheres in the steel at the point of impact, caused a solution of 71 per cent. sugar to crystallize out within 3° C. of the temperature of saturation; while Mr. Applebey gets the same solution out with the most rapid shaking only within 6°·5 of the crystallizing point.

(24) If we remember that increased rapidity of shaking means an increase in the force of impact, and that the pressure developed in my experiments is much greater than in Mr. Applebey's, we may, following Young, state that the greater the blow the closer we can bring the supersolubility to the solubility curve. Assuming that the solutions are on

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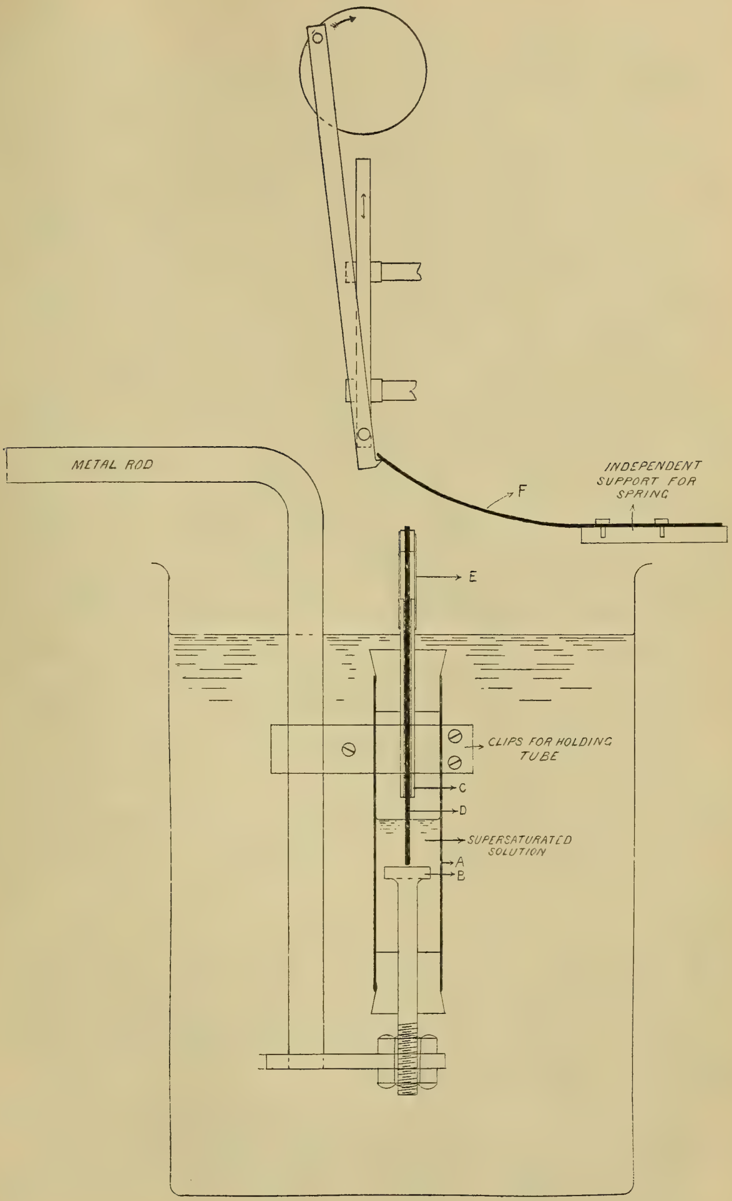
* Miers and Miss Isaac, Harold Hartley with several collaborators, and others.

† Journal American Chem. Soc. vol. xxxiii. p. 148 (1911).

Fig. 6.


METAL ROD
INDEPENDENT SUPPORT FOR SPRING
F
E
CLIPS FOR HOLDING TUBE
C
D
SUPERSATURATED SOLUTION
A
B

the part of the curve EK of fig. 4, and postulating local deviations from the mean concentration ; then a simple explanation of these experiments is found in the fact that pressure-rarefaction waves * of an amplitude amounting, perhaps, to many atmospheres, travelling outwards from the point of impact, are set up in the solution; and these waves, when they pass over the local aggregations, will (if the pressure change is large enough) bring the latter to a point of instability analogous to K, after which the events taking place are similar to that already described in paragraph (18).

(25) It is to be noted that the effect is the same whether the solubility is increased or decreased by pressure ; in the first case it will be the defect of pressure in the wave which is effective, and in the second it is the increase of pressure. Young also found that with supercooled pure liquids the same law was operative, *i. e.* that the liquid solidified closer to the melting-point when the blow was greater. An explanation similar to the foregoing could easily be based on the assumption that there is no such thing as a pure liquid, the so-called pure liquid is only a liquid phase of very high concentration ; but this far-fetched hypothesis is probably not necessary, the known effect of pressure on the melting-point in conjunction with an assumed want of homogeneity in the liquid being sufficient to explain the phenomena.

I wish here to express my obligations to the gentlemen in my laboratory for suggestions and effective criticism, and especially to Dr. Burton for working out the two thermodynamic cycles and for other physico-mathematical help.

XXI. *The Influence of Density on the Position of the Emission and Absorption Lines in a Gas-spectrum.* By G. H. LIVENS, *B.A.*, *Fellow of Jesus College* †.

Introduction.

THE subject to be specifically discussed in this paper is the change of position of the lines in the emission and absorption spectra of a gas due to changes in its density. Certain effects on intensity will also be dealt with in the section on absorption spectra.

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* The waves will be accompanied by small thermodynamic heating and cooling effects which, in the case of the majority of aqueous solutions, will act in the same direction as the corresponding pressure changes.

† Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S., being the major portion of an essay which was awarded the first Smith's Prize in the University of Cambridge in March 1911.

The changes of position of the bright lines in the spectra of metals due to changes in "pressure" were first investigated by Humphreys and Mohler *. Their experiments were suggested by some remarks of Jewel, who noticed that the position of the metallic lines in the solar spectrum did not correspond exactly to the positions of the same lines in spectra obtained from an arc in the laboratory. In 1907 Humphreys published the complete results of a very extensive research carried out by himself on this subject †. His method consisted, generally speaking, in comparing the metallic spectra obtained from arcs surrounded by ordinary air at pressures varying between 1 and 100 atmospheres.

Theoretically very little has been done on the subject. Three distinct explanations have, however, been suggested. The earliest is that the phenomenon is due to the effect of damping of the vibrations to which the emission of light is due: this has been discussed at great length by Lommel and Wilsing ‡. The second and apparently much better suggestion explains the shift as due to the surrounding gas. Prof. Larmor, in a highly suggestive and interesting note in the 'Astrophysical Journal' (1907), attributes the shift to a change in the specific inductive capacity of the surrounding air. The third explanation bases the phenomenon on some curious magnetic properties of the atoms. This was done in order to explain some supposed connexion between the phenomenon here under discussion and the Zeeman effect.

I now propose to develop a theory which attributes the effect to a density change in the actual incandescent vapour. In another part of this paper I shall give my reasons for believing that in Humphreys' experiments an increase in the density of the incandescent metallic vapour takes place simultaneously with an increase in the pressure of the surrounding atmospheric air.

The theory here given is a simple explanation based on the electron theory of optical effects first started and systematically developed by Lorentz and Drude. The peculiarity of the work here presented consists mathematically in the introduction into the equations of motion of the single typical electron of a force on that electron due to the polarization in the surrounding medium. This term was, I believe, originally introduced by Lorentz, and by means of it he obtains the law (first discovered by Lorenz) connecting the

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* Astrophysical Journal, 1896.

† Astrophysical Journal, 1907.

‡ See Astrophysical Journal, 1893.

index of refraction μ of a simple gaseous substance with its density ρ, viz.

$$\frac{\mu^2-1}{\rho(\mu^2+2)}=\text{const.}$$

Physically the function of the new term seems to be expressed by saying that the presence of neighbouring electrons causes an increase in the effective inertia of the typical oscillating electron more particularly considered. In the words of Prof. Larmor[*]: "Each molecule individually, through the agency of its plastic field of force or æther strain, provides a yielding region in the æther in which the effective stiffness is diminished. The elastic energy which maintains the free vibrations of a radiator is located in the field of force in the adjacent æther, and by dynamical principles any loosening of the constraint in that field, such as an adjacent molecule would produce, which would itself be somewhat intensified by equality of period, must in general tend towards increasing the free period, involving displacement of the radiation towards longer wave-length."

The paper is divided into three sections: the first deals with absorption effects; the second with a theory of the emission effects ; and the third contains a quantitative comparison of the theoretical and experimental results. The results obtained in the first section showed such a remarkable similarity with the experimental results obtained for the emission spectra that I was induced to construct the theory presented in the second section.

Throughout the work I have followed, with Lorentz, the Hertz-Heaviside choice of mixed units. The unit of electricity adopted is therefore $\sqrt{4\pi}$ times smaller than the usual electrostatic unit.

I might here also express my indebtedness to the various works and papers of the following authors : Lorentz, Voigt, Drude, Larmor, and Campbell. Verbal quotations have often been adopted from them.

I. *General Theory for the Absorption Spectrum.*

§ 1. *The fundamental basis.*—The whole theory of electro- and magneto-optics is based on the fundamental laws of electrodynamics. These are

1. *Ampère's Circuital Relation.*

The line integral of magnetic force round any circuit is equal to $\left(\frac{1}{c}\right)$ multiplied into the *total* electric flow through its aperture.

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[*] Astrophysical Journal, 1907.

[c denotes the velocity of radiation, and is introduced conformably to the units adopted.]

The line integral of magnetic force means that we take the tangential component of the force, multiply it by the element δs of length of the circuit, and then add up all round.

The above statement of the first relation could have no meaning unless the electric flow were a stream vector; there must be no accumulation; the current can have no convergence. The flow through the aperture means the flow across some surface which abuts on the aperture, and must be the same for all such surfaces, otherwise the expression has no meaning. This states that all currents are circuital in the sense that if we take a tube of flow it is always full, and either comes back on itself or goes to infinity. If we define a current as a flow of electricity this is by no means always true. For example, in the discharge of a condenser with a vacuum dielectric we should have an open current. Maxwell's hypothesis, made to simplify the theory, was that even in this case some sort of release of strain in the æther takes place, which has the electrodynamic properties of a movement of electricity. It is not a movement of electricity!

It is shown in the theory of this subject that this fictitious current must be measured by the time rate of change of the electric force.

We have thus got to make a distinction between the true current, which is a true flow of electricity (or electrons) and this fictitious current in the æther. The contrast is between total and true current. The total current contains a part which is not true electric flow at all, but is a something possessing the electrodynamic properties of a true electric flow.

2. *Faraday's Circuital Relation.*

The line integral of electric force round a circuit is $\left(\frac{1}{c}\right)$ multiplied into the rate of decrease of the total induction through its aperture.

The relation implies that the tubes of magnetic induction are circuital: the total induction is the same whatever surface it is measured on. In the case of iron, nickel, or any magnetizable body, this brings in a distinction. If a magnetic metal were present the ordinary magnetic force is, as we know from elementary theory, not circuital, and this leads to a distinction between magnetic force and magnetic induction. The two are, however, practically the same, except in iron, and we shall not further distinguish between them.

The quantities involved in these two statements are:

1. Magnetic force (magnetic induction) H; (H_x, H_y, H_z).
2. Electric force .... E; (E_x, E_y, E_z).
3. Total current .... U; (U_x, U_y, U_z).

There are three (vector) quantities and only two relations between them. We want one more! The two relations given are independent of what the body is, and they might be called the fundamental dynamical equations. In addition to these there must be a constitutive relation of some kind connecting the quantities: it will depend essentially on the constitution of the body, and we must discuss this before we can form any idea as to what it is likely to be.

§ 2. *The physical conceptions of the body*: *constitution of the atom*; *introduction of the electron hypothesis.*—We imagine a body composed of innumerable molecules or atoms, of "particles," as Lorentz calls them, each molecule containing a certain number of "electrons." These electrons are now fairly well known elements of electrical and optical theories, and I shall not now enter into any discussion of their properties. As is now generally done in optical work, I shall regard them as "particles" (in an electrical interpretation of the Newtonian word) with a definite electromagnetic mass. This is, as we know, an assumption which is not really justified except in very special cases. It is only a very good approximation to the truth when the dimensions with which we deal are large compared with the dimensions of the nucleus comprising the electron; and also (and this is very important) when its velocity is small compared with that of radiation. These two assumptions are still very generally made in dealing with optical theories of matter, although some notable authorities disbelieve the justification of the step made in doing so. A very powerful argument in favour of making these assumptions is, however, that it enables us to go very deeply into the phenomena under discussion. It is not pretended that this is the last word on the subject, and our theory may have to be very considerably modified as our knowledge of facts broadens; but in the present state of science they are reasonable hypotheses, besides being the only ones with which we can to any extent work.

We now want to form some kind of idea as to what sort of system this atom with its electrons is. Of course any picture which may be imagined cannot in the least be said to depict things as they actually exist. All we do is to imagine some system that will coordinate and explain the majority of the phenomena known to us. For this reason we choose the hypothesis which has the advantage over all others in attempting to explain all physical and chemical phenomena by the properties of the one system, these negative electrons, which appear in the present state of knowledge to be the true "indivisible" atom. But since the chemical atom is, as a whole, electrically neutral, it is necessary to introduce somewhere a positive charge equal in magnitude to the total charge on the electrons. Since there is as yet no evidence as to the distribution of this charge, it is best to adopt an hypothesis which renders most easy the task of deducing the properties of the atom from its structure. It will be supposed, therefore, that the positive electrification is distributed rigidly throughout the volume of the atom, and that the whole atom consists of this volume distribution of electricity throughout which are distributed a number of electrons. The model atom, as pictured by Kelvin and worked with by J. J. Thomson, was assumed to be spherical in form and the distribution of the positive charge to be uniform, but we need not make these special assumptions for our present theory.

Now all optical phenomena are concerned with the oscillation of this complicated electrical system, called an atom, about a configuration of stable equilibrium. The oscillation is that of the electrons, at least when we are dealing with line spectra, and we discuss the subject in terms of electrons. However, any method of procedure in which the motion of the individual electrons is the object of our investigation, is wholly useless when, as in gaseous bodies and liquids, the distribution of the atoms is highly irregular. As Larmor says [*], "the development of the theory which is to be in line with experience must instead concern itself with an effective differential element of volume containing a crowd of molecules numerous enough to be expressible continuously, as regards their average relations, as a volume density. As regards the actual distribution in the element of volume of the really discrete electrons, all that we can usually take cognizance of is an excess of one kind, positive or negative, which constitutes a volume density of electrification, or else an average polarization in the arrangement of the groups of electrons in the particles, ... With anything else than the mean aggregates of the various types that can be thus separated out, each extended over the effective element of volume, mechanical science, which has for its object matter in bulk as it presents itself to our observation and experiment, is not directly concerned."

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[*] 'Æther and Matter.'

We have thus got to express ourselves in terms of statistical or averaged sums over all the electrons in the element of volume. Statistically the effect of an electric force on a body is to polarize the molecules, that is, to twist them round or alter them in some way so that they have a definite polarity. We can express this polarity as an averaged sum over all the electrons per unit volume.

The x-component of the moment of a simple bipolar element is

$$ex' - ex,$$

$(x' y' z')$ being the coordinates of the positive pole, and (x, y, z) those of the negative pole of the doublet referred to fixed rectangular axes.

If the element of volume is small enough we have simply to add up vectorially the moments of the simple doublets contained in it to get the resultant moment of the element, *i. e.* its polarization.

The x-component of the intensity of polarization is thus

$$\Sigma\, e(x' - x),$$

where Σ is taken *per unit volume* over all doublets. [The meaning of "per unit volume" is that we calculate the sum for the small element $d\tau$ and then divide the result by $d\tau$.]

This is seen to be $\Sigma\, ex$, taken for *all* electrons per unit volume, due regard being paid to sign. Thus

$$P_x = \Sigma\, ex$$

is the x-component of the intensity of polarization.

It may be here noticed that we have spoken of doublets formed of a negative electron and an equal and similar positive charge; whereas our assumptions on the "model" atom come to the fact that the positive electrification is distributed as a volume density throughout the atom. However, we are not concerned with the actual distribution of this positive charge in any particular form, and we may safely assume that it is distributed in such a way that we can conceive definite doublets in the above form. The only essential point is that the positive electricity is rigidly connected with the atom.

Now consider

$$P_x = \Sigma\, ex$$

taken for all the electrons and positive charges in the manner indicated. Let $(\bar{x}, \bar{y}, \bar{z})$ be the mean position of the positive charge in the element of volume at any instant, then, since the atom was originally neutral, this is also the mean position of the negative charges before they are displaced relatively to the positive charge. Thus $\Sigma\, ex$ for the positive charges is

$$\bar{x}\, \Sigma\, e,$$

and for the negative charges it is

$$\bar{x}\, \Sigma\, e + \Sigma\, ex,$$

where (x, y, z) is now the displacement of the negative electron e from its neutral position of equilibrium.

But $(\Sigma\, e)$ for the positive charges is equal but opposite in sign to $(\Sigma\, e)$ for the negative electrons, and thus we have

$$P_x = \Sigma\, ex,$$

Σ being now taken only for the negative electrons, (x, y, z) denoting the component displacements of that electron from its neutral position of equilibrium.

We have thus expressed the polarization in terms of the negative electrons alone, and it is in this form that we shall make use of it.

We shall now follow the procedure usually adopted in these theories. It is admirably set out by Lorentz in his book on electrons, and I follow him closely and often verbally.

§ 3. *Equations of motion of the electron.*—The position of the electron, or better its displacement (x, y, z), and therefore the polarization, depends on the forces acting on the electron. These forces are of four possible types.

(a) *Quasi-elastic forces.*—If the electron vibrates about any one position of equilibrium in a motion with a definite period, it must be acted on by some elastic resilience, tending to drag it into this position. We shall suppose a force of this kind exists, directed towards the position of equilibrium and proportional to the displacement from that position. If the displacement is small we can easily imagine the force to have its origin in the mutual electrical actions in the atom. If we denote by k a certain positive constant which depends on the properties of the atom, which may, however, be different for different electrons in the atom, we write for the components of the force

$$-kx,\ -ky,\ -kz$$

(x, y, z) being interpreted, as before stated, for each electron as the components in three definite directions of its displacement from the equilibrium position it occupied when the atom was undisturbed by any electrical actions.

(b) *Resistance to the motion.*—The second force is a resistance to the motion of the electron. We shall introduce some action of this kind because without it we could not possibly account for absorption. Following the example set by Helmholtz we shall put this as

$$-h\dot{x},\ -h\dot{y},\ -h\dot{z},$$

where h is some positive constant.

Lorentz, in his book, discusses the origin of this force very fully but rather abortively.

(c) *The force acting on the electron due to the electromagnetic field.*—We have now to consider the forces on the electron due to the electromagnetic field in the æther. At first sight it might be thought that this action is to be represented by eE, where E (a vector) is the electric force intensity, and this is what is taken by most authors. On closer examination one finds, however, that a term must be added on account of the polarization in the medium. The force in a polarized body depends on having a cavity in the body, and the result depends on the shape and not on the size of the cavity when small. In the theory of polarized media "the division of the forcive per unit volume into a molecular and a molar part is made by means of the ideal volume and surface densities of Poisson, which are the equivalent as regards outside points of the actual polarization of the material. The method consists essentially in computing the forcive by combining opposed poles of neighbouring elements instead of taking the single polarized element as the unit. It shows that these adjacent poles nearly compensate each other, except as regards a simple volume density whose attraction has no molecular part and a surface density partly at the outer surface and partly at the surface of the cavity which contains the point under consideration. The effect of the latter surface density, depending as it does wholly on the immediate surroundings, is the molecular or cohesive part of the average forcive . . . . . . The intensity of this local part of the regular force acting at an electron has been assigned as $\frac{1}{3}$P very approximately for the case of fluid media, possibly not so approximately for solids. [P is the vector defining the intensity of polarization in the medium at the point.] The argument was that owing to the translatory mobility of the surrounding molecules their action on the one under consideration averages into that of the uncompensated distribution of poles which would exist on the surface of a small spherical cavity in a continuous uniformly polarized medium"*. By a more general discussion Lorentz has arrived at the conclusion that the force may generally be taken as

$$aP,$$

in the direction of P, where a is some constant which depends on the local distribution of atoms or molecules at the point, and which would consequently vary with the temperature and pressure, but which in most cases is very nearly equal to $\frac{1}{3}$. I shall retain the constant a throughout the algebraical work, and use the value $a=\frac{1}{3}$ in the numerical calculations. In any case the way in which the constant a enters into the calculations will always be quite clear. The value $a=0$ brings us back to the older theory.

(d) *The magnetic force.*—The last of the forces to be here considered only occurs in discussions of the effect of an "external" magnetic field, denoted by H, and always considered as directed along the z-axis. Its action on the vibrating electron is represented by force components

$$-\frac{eH}{c}\dot{y}, \quad +\frac{eH}{c}\dot{x}, \quad 0.$$

A note should here be added in connexion with the forces discussed in paragraphs (*b*) and (*d*). Both of these forces are proportional to the velocity of the electron.

Now the velocity of the typical electron is not $(\dot{x}, \dot{y}, \dot{z})$ but $(\dot{x}+u, \dot{y}+v, \dot{z}+w)$, where (u, v, w) is the velocity of the molecule or atom in which the electron is to be found. This, of course, is a direct consequence of our previous interpretation of (x, y, z). We have, therefore, neglected two forces whose components may be written in the form

$$-(hu, hv, hw),$$

and

$$-\frac{eH}{c}(v, -u, 0).$$

Both of these forces would act on the electron independently of the forces due to the electrodynamic field considered in the optical case; the latter, of course, depends on the constant external magnetic field, which is present when we are dealing with the Zeeman effect.

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* Larmor, Phil. Trans. 1897.

These forces would account for a slight displacement of the electron from what we have described as its absolute and neutral position of equilibrium in the atom or molecule, the displacement in the latter case probably being a vector one related to the direction of the magnetic field. The displacements would depend on the motion of the molecule, being therefore different for different molecules, but would be independent of any of the optical effects to be discussed. If we transfer the origin of (x, y, z) from the absolute to this displaced position of equilibrium we obtain exactly the same equations of motion as before, provided that the acceleration of the molecule is small compared with that of the electron contained within it. This is a legitimate hypothesis to make for the case of a gaseous substance where the greater part of the motion of a molecule is linear and undisturbed by any action.

In any case we can, however, neglect the effects of these forces in adopting a statistical theory of the subject. The velocity of the molecule is just as likely to be $-(u, v, w)$ as $+(u, v, w)$, and on the average will be zero. In any case a retention of these terms could merely account for a broadening of the line about the absolute position, if we consider that a slight displacement of the electron in the molecule alters its free period of vibration.

We shall neglect the effects of these forces so that we can still confine our discussion to the consideration of the negative electrons alone. The above four kinds of force cover all those we can imagine to act on the electron in any ordinary case, and with them the equations of motion of the electron are of the form

$$m\ddot{x} = e(\mathrm{E}_x + a\mathrm{P}_x) - \frac{e\mathrm{H}}{c}\dot{y} - h\dot{x} - kx,$$

$$m\ddot{y} = e(\mathrm{E}_y + a\mathrm{P}_y) + \frac{e\mathrm{H}}{c}\dot{x} - h\dot{y} - ky,$$

$$m\ddot{z} = e(\mathrm{E}_z + a\mathrm{P}_z) \qquad\qquad - h\dot{z} - kz.$$

If now the light incident on the body is a simple harmonic wave-train of frequency n, the electrons are compelled, with more or less success, by the electric force in the incident wave to vibrate with a period $\frac{2\pi}{n}$. Thus if the functions depend on the time by the imaginary exponential factor e^{int} we have

$$(-mn^2+ihn+k)x=e(E_x+aP_x)-\frac{ieHn}{c}y,$$

$$(-mn^2+ihn+k)y=e(E_y+aP_y)+\frac{ieHn}{c}x,$$

$$(-mn^2+ihn+k)z=e(E_z+aP_z).$$

By solving these equations for (x, y, z) we get the position of the typical electron corresponding to the values E of the electric force and P of the polarization. By forming the sums $(\Sigma ex, \Sigma ey, \Sigma ez)$ per unit volume we obtain, since they are respectively equal to (P_x, P_y, P_z), three linear relations between the components of the electric force and of the intensity of polarization, the coefficients being in general complex functions of the frequency of the periodic light disturbance considered. From these equations we can determine a relation between the electric force intensity and the polarization intensity. It comes out of the form

$$P=4\pi\sigma E,$$

where σ is in general complex, depending on the constitution of the substance and the frequency of the light used.

This is the third relation required, connecting the quantities involved in the fundamental equations. The relation does not, however, connect quantities which explicitly occur in the fundamental differential equations of the theory in the form in which we have taken. In fact it involves a new vector, the polarization which does not appear in the fundamental equations at all. We can, however, easily connect the polarization P with the true electric current.

The true flow of electricity is easily expressed. It can be seen to be a vector equivalent to the vector whose components are

$$\Sigma e\dot{x}, \Sigma e\dot{y}, \Sigma e\dot{z},$$

Σ being taken per unit volume over the negative electrons, due regard being paid to the meaning of (x, y, z). But this is the vector

$$\dot{P},$$

which is, therefore, the true current. The total current U consists of this true flow of electricity, together with a fictitious current due to a supposed change of the elastic state of the æther. This latter current is shown to be expressed by the time rate of change of the electric force intensity, viz. $\dot{\mathrm{E}}$, and therefore the total current is

$$\mathrm{U}=\dot{\mathrm{P}}+\dot{\mathrm{E}}=(1+4\pi\sigma)\dot{\mathrm{E}}$$
$$=\mathrm{K}\dot{\mathrm{E}}=in\mathrm{KE},$$

and this is the relation that is really required. It is like a generalized Ohm's law, and depends essentially on the constitution of the substance under consideration.

With the two fundamental electrodynamic equations and this constitutive relation we have a sufficient number of equations to enable us to proceed to a complete analysis of the electrodynamic field in the body when the given wave-disturbance passes through it.

§ 4. *Mathematical formulæ: their reduction to the optical case.*—We have the following mathematical relations between the vectors involved in the theory:—

$$\int(\mathrm{H}_x dx+\mathrm{H}_y dy+\mathrm{H}_z dz)=\frac{1}{c}\iint(l\mathrm{U}_x+m\mathrm{U}_y+n\mathrm{U}_z)d\mathrm{S},$$

$$\int(\mathrm{E}_x dx+\mathrm{E}_y dy+\mathrm{E}_z dz)=-\frac{1}{c}\frac{d}{dt}\iint(l\mathrm{H}_x+m\mathrm{H}_y+n\mathrm{H}_z)d\mathrm{S},$$

giving in the usual vector notation

$$\frac{1}{c}\mathrm{U}=\mathrm{Curl\ H},\quad -\frac{1}{c}\dot{\mathrm{H}}=\mathrm{Curl\ E},$$

with $$\mathrm{U}=in\mathrm{KE}=\mathrm{K}\dot{\mathrm{E}}.$$

We shall now examine the propagation of the light in a medium where these equations are satisfied. In order to simplify the general equations we adopt a standard convention, to which we shall always adhere. We consider the propagation of plane homogeneous waves taking place in the direction of the axis Oz, so that the components of E, H, and U involve the coordinates of space and time by the exponential factor $e^{in(t-qz)}$, where q is in general a complex quantity, a function of n the frequency of the light disturbance.

Now since all differentials with respect to x and y vanish, the general equations reduce to

$$inq\mathrm{H}_y=\frac{1}{c}\mathrm{U},\quad q\mathrm{E}_x=\frac{1}{c}\mathrm{H}_y.$$

Thus for the propagation of this wave-train to be possible in the medium we must have

$$q^2c^2=\mathrm{K}.$$

Now in the general case K is imaginary, and it is then that q is imaginary and absorption results. Suppose

$$cq=\mu(1-i\kappa),$$

where μ and κ are real; the exponential factor is then

$$e^{-\frac{\mu\kappa z}{c}}e^{in\left(t-\frac{\mu z}{c}\right)}.$$

We see that $\left.\frac{c}{\mu}\right)$ is the velocity of the disturbance in the medium, and therefore μ is the ordinary index of refraction of the medium. The absorption is determined by $(\mu\kappa)$, which may be called the index of absorption. We have now

$$\mu^2(1-i\kappa)^2=\mathrm{K},$$

and this is the important relation. We know K and can thus determine μ and $\mu\kappa$, and from the latter deduce all the circumstances of the absorption. We shall now proceed to a detailed discussion of this relation in the several cases.

§ 5. *Absorption in the neighbourhood of a line in the spectrum.*—The method pursued in this and the following paragraphs follows very closely that given by Voigt in his book 'Magneto- und Electro-Optik,' and I refer the reader to that book for a fuller discussion of the algebraical processes involved.

We first discuss the ordinary absorption phenomenon without the action of an external magnetic field. The frequency of the incident disturbance being n we have for the typical electron

$$(k+ihn-mn^2)x=e(\mathrm{E}_x+a\mathrm{P}_x),$$

and two similar equations; say

$$px=e(\mathrm{E}_x+a\mathrm{P}_x).$$

Now eliminate the single electron by adding up per unit volume over all the electrons in a differential element of volume, obtaining the polarization as a statistical sum

$$\mathrm{P}_x=\Sigma\, ex=\mathrm{E}_x\Sigma\frac{e^2}{p}+a\mathrm{P}_x\Sigma\frac{e^2}{p},$$

or

$$\mathrm{P}_x\left(1-a\Sigma\frac{e^2}{p}\right)=\mathrm{E}_x\Sigma\frac{e^2}{p}.$$

We have thus the value for K or $\mu^2(1-i\kappa)^2$, viz.

$$\mu^2(1-i\kappa)^2=\mathrm{K}=1+\frac{\Sigma\frac{e^2}{p}}{1-a\Sigma\frac{e^2}{p}}.$$

Lorentz has considered this formula for μ at parts of the spectrum where the absorption is negligible, that is between the spectrum lines. Natanson has extended Lorentz's results for similar cases, and applied the theory to a large number of practical cases. I propose to consider the formula more particularly in the neighbourhood of a line in the spectrum of the substance under consideration, where the absorption is no longer negligible.

We consider the formula near the absorption band determined by the natural free period $n=n_0$ of a group of electrons. Let N_1 be the number of electrons per unit volume with this period as the natural one. As we are dealing with the region near $n=n_0$ only, we put $n=n_0+\xi$ and neglect high powers of ξ, and thus

$$p_1=-m_1 2n_0\xi+ih_1n_0.$$

We adopt the notation

$$\rho_1=\frac{\mathrm{N}_1e^2}{m_1},\quad n'=\frac{h_1}{m_1},$$

and

$$\mathrm{A}=\Sigma\frac{e^2}{k-mn_0^{\,2}},$$

Σ referring to all the electrons not included in N_1.

Adopting all the approximations usual to this theory, as set out in Prof. Voigt's book, we get

$$\mu(1-i\kappa)=1+\frac{1}{2}\frac{\mathrm{A}(-2n_0\xi+in'n_0)+\rho_1}{(1-a\mathrm{A})(-2n_0\xi+in_0n')-a\rho_1},$$

whence

$$\mu\kappa=\frac{1}{2}\frac{\rho_1n'n_0}{[(1-a\mathrm{A})2n_0\xi+a\rho_1]^2+(1-a\mathrm{A})^2n'^2n_0^{\,2}}.$$

This agrees with the usual formula obtained if we put $a=0$. Moreover, for the gas A is small and we can write

$$\mu\kappa=\frac{1}{2}\frac{n'n_0\rho_1}{(2n_0\xi+a\rho_1)^2+n_0^{\,2}n'^2}.$$

The last approximation merely means that each spectrum line is, as far as its position and intensity are concerned, practically independent of the other lines in the same spectrum.

The centre of the band, the place of maximum absorption, occurs at the position

$$\xi = -\frac{a\rho_1}{2n_0}.$$

The maximum value of the absorption coefficient is

$$\mu\kappa = \frac{1}{2}\frac{\rho_1}{n'n_0}.$$

The positions in the spectrum where the intensity is one half its maximum value are given by

$$\xi = -\frac{a\rho_1}{2n_0} \pm \frac{n'}{2}.$$

The first of these results is really the only one which differs essentially from that given in the usual theory. The position of the absorption band does not actually correspond to the natural period $n = n_0$ of the group of electrons concerned, but is displaced from this position through a distance $\xi = -\frac{a\rho_1}{2n_0}$, measured on the frequency scale. Now

$$\rho_1 = \frac{N_1 e^2}{m} = (N_1 m)\left(\frac{e}{m}\right)^2.$$

Thus ρ_1 is proportional to the density of the electrons of the N_1 group. This is assumed to be proportional to the ordinary density of the gas.

We have thus shown that the spectrum line is displaced from its absolute position given by $n = n_0$. The displacement is towards the red end of the spectrum (greater wave-length or smaller frequency), and is directly proportional to the density of the gas. It is different for different lines, being proportional to the density of the electrons which give rise to each line.

§ 6. *The inverse Zeeman effect.*—I have applied the foregoing principles to the theory of the simple Zeeman effect, and to a simple case of Voigt's theory of the complicated effect.

The algebraical work is much the same as that just given, and I shall content myself with quoting results as the method of obtaining them is now obvious.

Under the action of an external magnetic field H the single line splits up into the ordinary symmetrical triplet with the separate lines in positions given by

$$\xi = -\frac{a\rho_1}{2n_0}, \quad \xi = -\frac{a\rho_1}{2n_0} \pm \frac{1}{2}\frac{eH}{cm},$$

their intensities all being $\frac{1}{2}\frac{\rho_1}{n_0 n'}$.

The theory thus accounts for a symmetrical Zeeman triplet in the ordinary way, but shifted in the manner of the single line, according to the theory at present under discussion, towards the red end of the spectrum. The shift is equal to that of the single line.

The results obtained by extending this theory to even the simplest case of Voigt's theory are complicated, but they lead to some interesting conclusions, which justify a consideration of them.

Voigt's notation is adopted, and the simple case of two "bound" electrons worked out. Adopting the notation $\rho_1 = \frac{Ne^2}{m}$ as before, with $\rho_2 = \frac{n_0 f}{m}$ and $n' = \frac{h}{m}$ we get for the resolution in the z-wave the two lines in positions given by

$$2n_0\xi = -\frac{a\rho_1}{2} \pm \sqrt{\frac{a^2\rho_1^2}{4} + \rho_2^2}.$$

The maximum intensities being

$$\frac{1}{2}\frac{\rho_1}{\sqrt{a^2\rho_1^2 + 4\rho_2^2}} \times \frac{\frac{a\rho_1}{2} \mp \sqrt{\frac{a^2\rho_1^2}{4} + \rho_2^2}}{n_0 n'}.$$

The mean position of the two lines is always at

$$\xi = -\frac{a\rho_1}{4n_0},$$

and the distance between them,

$$\frac{\sqrt{a^2\rho_1^2 + 4\rho_2^2}}{2n_0},$$

increases from $\left(\frac{a\rho_1}{2n_0}\right)$ to infinity with increasing magnetic field. ρ_2 is proportional to H.

These results are certainly remarkable. The single line is separated by the magnetic field into two lines at equal distances from the position $\xi = -\frac{a\rho_1}{4n_0}$, but of unequal intensity. One of these lines would be invisible in a small magnetic field, but in a strong magnetic field the two lines would be of equal intensity. Moreover, the separation produced by the magnetic field is superposed in the manner above indicated on an initial distance $\left(\frac{ap_1}{2n_0}\right)$ apart of the two lines; this distance is precisely that calculated as the pressure shift of the single line, and so we can assert that those lines which show a good pressure shift will also show a good separation of the lines under the action of a magnetic field, as the separation always starts with this initial value. Similar conclusions are obtained by considering the other components of the wave oscillation (Voigt's S-wave). I have worked this case out, but the results exhibit nothing new, and I shall not repeat them here.

II. *Theory for Emission Spectrum.*

I now propose to construct a theory for the emission spectrum corresponding to the absorption theory just developed. Experiment indicates that the emission and absorption lines are exactly similarly affected in this respect. It will, however, first be necessary to discuss the subject of the emission of the light disturbance by a gas rather more fully.

As we have previously shown, the subject can be discussed in terms of the real negative electrons, neglecting altogether the positive charge and its motion. There are of course certain effects which can be attributed to these two causes, such, for instance, are the phenomena of band-spectra and a definite width of the lines in line spectra. These matters are, however, independent of the subject under consideration, and may be left out of account in the discussion.

We thus confine the discussion to the negative electrons, typified by the electron with a charge e, whose displacement from its position of equilibrium in the atom is determined by the vector whose components are (x, y, z) referred to fixed directions in space.

Now consider the emitting gas (or vapour) as a whole, and take any volume element $d\tau$ of it, which contains a crowd of molecules numerous enough to be expressible continuously. We can investigate the radiation from this element in terms of the oscillating electrons in the molecules in it.

Now Larmor has shown that there is no radiation from the element if a certain condition holds, which condition is equivalent in our case to

$$(\Sigma e\ddot{x},\ \Sigma e\ddot{y},\ \Sigma e\ddot{z})=0,$$

always. The sum Σ being in each case taken over all the negative electrons in the element $d\tau$. It should be noted that this is not precisely the way Larmor states the condition. The coordinates (x, y, z) are not the absolute coordinates of the electron, but coordinates relative to the moving molecule. However, as both the positive charges and negative electrons partake of the motion of the molecules in emission, and as they are paired in equal quantities in the neighbourhood of certain fixed points in the molecule, we see that the contribution to the sum Σ in Larmor's case, due to the motion of the molecules, would vanish, and we should be left with the result as stated.

But $$\Sigma\,(e\ddot{x},\ e\ddot{y},\ e\ddot{z})=(\ddot{\mathrm{P}}_x,\ \ddot{\mathrm{P}}_y,\ \ddot{\mathrm{P}}_z)\,d\tau,$$

where P is a vector expressing what we may still describe as a polarization in the element $d\tau$. It is exactly analogous to the polarization in our previous theory.

The statement is therefore equivalent to saying that there is no radiation from the element if

$$(\ddot{\mathrm{P}}_x,\ \ddot{\mathrm{P}}_y,\ \ddot{\mathrm{P}}_z)\,d\tau=0$$

continuously.

Thus we conclude that if we are to obtain any radiation from the element $d\tau$ at all, it must be polarized electrically. The vapour, of course, on the whole exhibits no signs of polarization, except those arising from the phenomena of its radiation. The polarization in the various elements of the vapour will be different in both direction and magnitude, and also continuously changing, the statistical result for the whole body being that it is not polarized. We have thus got a state of affairs analogous to that which was pictured and used to explain the older theories of dielectric polarization. The substance was supposed to contain innumerable polarized elements which, in the absence of any directive force, were scattered indiscriminately and turned in all sorts of directions, thereby neutralizing one another's effects, and leaving the body as a whole unpolarized.

Now if the element $d\tau$ is polarized to an intensity P, there is a force aeP acting on any electron in the element. The force aeP in the equations of motion of the electron, as previously given, was seen to arise from the local polarized distribution of molecules and electrons about the one under consideration, and will therefore exist in our case, even though the gas is not polarized as a whole. This is the local effect, and depends solely on the local conditions, and from this point of view the body is polarized. It is, of course, a statistical measurement of the effect. We do not, and cannot, take any account of the very possibly large variation in the local forces. We average them up and express the result statistically.

The equations of motion of the typical electron in the element are thus all like

$$m\ddot{x}+h\dot{x}+kx=ea\mathrm{P}_x.$$

The forces governing the motion being exactly the same as in the previous case, with the single exception that there is no electric force E acting.

But according to experiment, light coming from a flame may maintain its capability of interfering after a distance of paths of a million wave-lengths, and so we may assume that the single emitting electron maintains its motion through a very large number of periods. We can thus neglect the resistance terms in these equations, and they then become like

$$m\ddot{x}+kx=ea\mathrm{P}_x.$$

To obtain the possible periods of the light disturbance which can proceed from the volume element $d\tau$ we proceed in the manner usual in such problems. Assume the quantities depend on the time by the factor e^{int}, and then

$$(-mn^2+k)x=ea\mathrm{P}_x.$$

Thus summing up per unit volume over all the electrons in the volume element $d\tau$ we get

$$\mathrm{P}_x=\Sigma\, ex=\mathrm{P}_x\Sigma\frac{ae^2}{k-mn^2}.$$

We thus deduce

$$1=\Sigma\frac{ae^2}{k-mn^2},$$

and thereby eliminate all ideas of any vector effect in the volume element $d\tau$. This result is true for any intensity and direction of polarization in the element.

This is the period equation for the oscillations in the light disturbances obtainable from the element or, since the element is merely a typical one, it is the period equation of the light emitted from the substance.

If we divide the different electrons present into groups according to their natural free period $n_0=\sqrt{\frac{k}{m}}$, and if N denote the number of electrons in the typical group per unit volume, then the equation is

$$1=\Sigma\frac{\mathrm{N}ae^2}{k-mn^2},$$

where Σ is now taken only over the different groups of electrons present. This can be written in the form

$$1=\Sigma\frac{a\rho}{n_0{}^2-n^2},$$

where

$$n_0{}^2=\frac{k}{m}, \text{ and } \rho=\frac{\mathrm{N}e^2}{m}=(\mathrm{N}m)\left(\frac{e}{m}\right)^2.$$

We thus see that the periods of the vibrations of which the system of electrons is capable are modified from the values they would have if each electron were quite free and unhampered by the presence of the other molecules.

If there is only one group of electrons present in the substance the period of vibration of the light obtainable from it would be given by

$$1=\frac{a\rho}{n_0{}^2-n^2},$$

$$n=\sqrt{n_0{}^2-a\rho},$$

or as the term $a\rho$ turns out to be small compared with n_0, we have approximately

$$n=n_0-\frac{a\rho}{2n_0}.$$

Now $\rho=(\mathrm{N}m)\left(\frac{e}{m}\right)^2$, and therefore depends on the density of the electrons present, that is on the density of the gas. Thus the period of a single oscillating electron, or at least the period of the light disturbance obtained from a system of such electrons, increases with an increase in the density of the gas in which the oscillations take place. An increase in the density of the incandescent gas or vapour shifts the lines towards the red end of the spectrum, that is increases the wave-length of the light emitted. The displacement is in all cases proportional to the change in the density, but may be different for different lines, depending on the density of the electrons giving rise to the line.

The displacement is exactly the same as that produced by the same effect in the absorption spectrum (see the previous section).

I have applied the theory here developed to other cases of emission spectra, including cases of the direct Zeeman effect. The results obtained were merely an adaptation of those previously obtained for the absorption spectra, and I do not consider it necessary to reproduce them here.

III. *Numerical.*

It might be as well to enter now into a comparison of the results obtained with the experimental facts; to show that the effects here discussed have some connexion with the actual ones. The comparison is, however, imperfect, as it is not between results for the same substances.

The numbers and results here quoted are derived from papers by Natanson in the Cracow Bulletin, and by Humphreys, Haschek and Mache in the 'Astrophysical Journal.' Natanson has applied experimental results to Lorentz's theory of absorption in a large number of cases extending over several gases. He was thus enabled to calculate the numerical values of the constants occurring in the absorption formula for the gases considered.

The displacement of the lines on our theory was given by a change in frequency dn_0, where

$$dn_0 = -\frac{a\rho}{2n_0},$$

and

$$\frac{dn_0}{n_0} = -\frac{a}{2n_0^2}\left(\frac{Ne^2}{m}\right).$$

Natanson uses the notation

$$\Delta = 3\pi c^2\frac{m}{Ne^2}, \quad D = \frac{\Delta}{\lambda_0^2}, \quad \lambda_0 = \frac{2\pi c}{n_0},$$

and in this notation

$$\frac{dn_0}{n_0} = -\frac{a}{2\Delta}\cdot\frac{3\pi c^2\lambda_0^2}{4\pi^2c^2} = -\frac{3a}{8\pi}\cdot\frac{1}{D}.$$

Also

$$\frac{d\lambda_0}{\lambda_0} = -\frac{dn_0}{n_0} = \frac{3a}{8\pi}\cdot\frac{1}{D}.$$

Now Natanson has calculated D for several gases in a large number of cases. The mean of some of his values give for

1. Hydrogen ...... $D=10907$
2. Oxygen .... $D=5360$
3. Nitrogen .... $D=4870$

These values are calculated for the gases mentioned under standard conditions of temperature and pressure. They were also made on the assumption that the gases are optically simple, that is that their absorption spectra consist of only one or two definite lines. Although for most gases this is not quite true, yet the results obtained will enable us to arrive at the order of magnitude of the quantities required, as the following argument will show. Natanson's experiments were made with monochromatic light of different wave-lengths. From the formula

$$\frac{\mu^2-1}{\mu^2+2}=\Sigma\frac{\rho}{n_0{}^2-n^2},$$

we see that for light of a given frequency the principal terms on the right-hand side are those which arise from the very limited number of groups of electrons (each group corresponding to a definite spectrum line) whose free natural periods are approximately equal to n, that of the light used. Thus the $\left(\frac{\mathrm{N}e^2}{m}\right)$ of our formula, which refers to the electrons giving rise to a single line, is of the same order of magnitude as that given by Natanson's formulæ, and therefore the order of magnitude of the shifts can be deduced from these results.

We use $a=\frac{1}{3}$, and then we have the displacements in the three gases as follows :—

1. Hydrogen ...... $\frac{d\lambda_0}{\lambda_0}=3{\cdot}6\times10^{-6}$ approx.
2. Oxygen .... $\frac{d\lambda_0}{\lambda_0}=7{\cdot}2\times10^{-6}$ approx.
3. Nitrogen ...... $\frac{d\lambda_0}{\lambda_0}=8\times10^{-6}$ approx.

Now what are the facts ? Unfortunately very little information is available with regard to the shifts of the lines in the spectra of either of the three gases we have just considered. Wilsing once obtained what he considered a reasonable estimate of the displacement of the hydrogen

β-line in an arc-spectrum. His estimate gives a value $(d\lambda/\lambda)=4.10^{-6}$, and this agrees with the figures given above, at least in order of magnitude.

Much more precise, however, is the information contained in Humphreys' papers in the Astrophysical Journal (see especially that in 1907). He has there given very numerous results for the metallic lines, and a comparison with these may be helpful.

In the first instance the phenomenon was first noticed when the arc spectra of certain metals were compared with the solar spectrum. The corresponding lines in the two did not occupy exactly the same positions. It was concluded that this was a pressure effect, and Humphreys tested the result by comparing the arc spectra of the metals when obtained in ordinary atmospheric air at different pressures (varying between 1 and 100 atmospheres). He summarizes his results verbally, and I append a few of his conclusions.

1. The brilliance of the arc becomes much greater at greater pressures.

2. The wave-lengths of all lines (except carbon) examined increased approximately proportional to the increase in the pressure, up to the highest pressures used, though this increase or shift is very different, not only for different elements, but even for different lines of the same element.

3. The amount of shift of a given line is practically independent of whether it is reversed: that is, the emission and absorption lines are similarly and equally affected.

4. In general the pressure shift of the spectrum lines seems to increase with the wave-length, but probably this is true only of the lines of the same series.

5. In general those lines which are strongly separated by a magnetic field are correspondingly largely displaced by pressure and conversely, those like lines of bands, that have but little if any Zeeman separation, are but slightly, if at all, shifted by pressure.

Humphreys' results, covering an enormous number of bands and several substances, show a large range of values for the shift. His figures give shifts ranging from $(d\lambda/\lambda)=1{\cdot}4\times10^{-5}$ down to $(d\lambda/\lambda)=5\times10^{-7}$. This easily covers the range in which our theoretical determinations fall.

The question may, however, be asked: what have our theoretical results to do with those experimentally investigated by Humphreys? It will be noticed that the pressure in his case was that of an inert or inactive gas, the air, surrounding the arc: this air was in quite an ordinary condition, at least at a distance from the arc. Our theoretical considerations do not cover any case of the kind here apparently presented: the action of a surrounding optically inactive gas was not considered at all in our theory, and even if it had been adopted it would have given no effect. According to the explanation given by us, we require an increase in the density of the incandescent vapour in the arc to give the effects under discussion.

It will, however, be noticed how well our results agree with those obtained by Humphreys. Our shift of the lines is equal in order of magnitude to that investigated by him. His conclusions given in paragraphs 2, 3, and 4 are exactly fulfilled by our theoretical shift, and we have found evidence that the conclusion drawn in paragraph 5 may also be fulfilled. It suits the case so well that I was induced to try and connect the two. The question now is: can an increase in the density of the incandescent vapour take place when the pressure in the surrounding air is increased? Certain evidence can be brought forward to answer this question in the affirmative.

In some experimental work on this subject Haschek and Mache* considered that they had obtained a demonstration of a high pressure in the path of the metallic arc, which may be considered as due to the metallic vapour thrown off from the electrodes. A further result, and the important one from our point of view, was the dependence of the pressure upon the pressure of the surrounding gas. The experiments were, however, conducted with pressures below that of the ordinary atmosphere (550 mm. to 96 mm.). Numerically the results obtained were rather irregular, but they indicate decisively that the pressure in the spark increases with that in the surrounding gas. The temperature of the arc being considered as constant, this means that an increase in the density of the metallic vapour is brought about by increasing the pressure of the surrounding gas.

Further and more direct evidence can also be obtained. For instance, in Humphreys' experiments it was found that the electrodes burn away much faster as the pressure is raised, and thus there is a greater rate of supply to the arc of the material to which the lines are due. This is equivalent to saying that the density of the metallic vapour in the arc is greater, or the temperature being practically constant, the pressure is greater. Humphreys accounts in this way for the increased intensity of the lines as described in conclusion 1. Again, Humphreys found that reversals are much more pronounced and frequent under heavy than under light pressures. To account for this he assumes that there must be a denser layer of absorbing vapours surrounding the arc under the heavier pressures. He thus introduces a density change in part of the metallic vapour, and it does not require much extension of the assumption to say that this change permeates the whole of the vapour in the arc.

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* Astrophysical Journal, 1879.

There seems, therefore, to be a fair amount of evidence to justify the assumption that an increase in the density (or pressure at constant temperature) of the metallic vapour in the arc corresponds to an increase in the pressure of the surrounding atmosphere. The evidence is, however, only qualitative. If the theory here developed accounts for the Humphreys' pressure shift, as determined in his experiments, we must conclude that the pressure of the metallic vapour is proportional, if not equal, to the pressure of the surrounding atmosphere. This fact is not quite in agreement with the results obtained by Haschek and Mache, but their experiments were conducted at very low pressures, and are hardly suitable to use quantitatively in any discussion referring to Humphreys' experiments where the pressure of the surrounding air varied between 1 and 100 atmospheres.

If, however, there is this change in density in Humphreys' experiments then the phenomena investigated by him would seem to admit of the simple explanation of the shift in the lines here developed.

XXII. *Note on Ionization Power of Negative Ions by Collisions at High Pressures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a recent paper * Mr. E. S. Bishop has published results giving the number of fresh ions α produced per cm. by negative ions in air, hydrogen, and carbon dioxide under various pressures and electric forces. Taking the electric force as X volts per cm. and measuring p in mm. of mercury the range of values of $\frac{X}{p}$ covered in this paper is from 45 to 70 for air, 20 to 70 for hydrogen, and 40 to 90 for carbon dioxide.

The values previously obtained by Professor Townsend † were obtained for very much lower pressures, and the values of $\frac{X}{p}$ were in general very much higher: for air 100 to 1000, hydrogen 30 to 400, carbon dioxide 100 to 1200.

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* Phys. Rev. xxxiii. p. 325, Nov. 1911; *Phys. Zeitschr.* xii. p. 1148, Dec. 8, 1911.

† 'Theory of Ionization of Gases by Collision.'

Remembering that $\frac{\alpha}{p}$ is a function of $\frac{X}{p}$, it is only possible to compare these results in the case of hydrogen, as is done in the following table:—

	$\frac{X}{p}$	30	50	70
$\frac{\alpha}{p}$	Townsend	·08	·36	1·0 *qp*
	Bishop	·054	·29	·59

from which it appears that the values obtained by Bishop are smaller than those previously obtained. Even where no values of $\frac{X}{p}$ are common, as for air, by plotting $\frac{\alpha}{p}$ against $\frac{X}{p}$ it is possible to see that the curves obtained by Townsend and Bishop cannot possibly join up, that of Bishop being again the lower. To account for this discrepancy it is necessary to consider the methods of finding α in the two cases.

Both start from the fundamental relation that if n_0 ions start from a negatively charged plate, the number reaching a parallel plate at distance d is given by

$$n = n_0 e^{ad},$$

it being assumed that only the negative ions are effective in producing fresh ions by collision. In both methods the n_0 ions are produced by ultra-violet light falling on a zinc plate.

The difficulty of finding n_0 was evaded by Townsend, who worked with two different distances, d_1, d_2, from which, if n_1, n_2 are the corresponding values of n,

$$\frac{n_1}{n_2} = e^{\alpha(d_1 - d_2)},$$

an equation giving α.

Bishop, on the other hand, obtained experimentally a complete current-E.M.F. curve, keeping d constant, and attempted to estimate n_0 from the saturation portion of this curve.

The ordinates of the rest of the curve then gave n for the corresponding X.

An inspection of his curves shows that this method is open to grave objection, for in no case is the saturation curve parallel to the axis of X, and it is therefore very difficult to tell where the saturation curve ends and the ionization curve begins. The possible percentage error in n_0 is large, and therefore the possible error in α is also large.

In order to test the accuracy of the results thus found in the case of air, some of his values of α have been redetermined by Townsend's method, using the actual pressures and electric forces employed by Bishop.

The currents between two parallel plates were measured in the ordinary way (see 'Theory of Ionization of Gases,' page 5), the distances chosen being 1, 2, 3, and in some cases 4 mm.

The ratios of successive readings should therefore be constant, and if r is the value of this constant,

$$\alpha = 10 \log_e r.$$

An investigation of a table of natural logarithms shows that for values of r up to about 1·6 the variation of $\log_e r$ is extremely rapid compared with the variation of r, and therefore a slight error in the determination of r involves a large error in α.

For instance, if

$$r = 1{\cdot}1, \quad \alpha = {\cdot}95,$$

and if

$$r = 1{\cdot}2, \quad \alpha = 1{\cdot}8.$$

No attempt was therefore made to measure the lowest values of α given by Bishop, while, on the other hand, sufficient volts were not obtainable to measure his highest values.

The results obtained were (for air) :—

Pressure in cms.	Force in volts per cm.	Ratio r.	a.	Value obtained by Bishop.
2·64	1806	1·92	6·52	4·16
2·64	1935	2·47	9·04	5·21
4·92	3010	2·2	7·97	3·06

The values of the ratio r were in all cases found to agree for successive distances within errors of experiments; and it will be seen that the values of α obtained are all considerably higher than those of Bishop. Even allowing the possibility of an error as large as 10 per cent. in the values of r, the values of α could only be reduced to 5·5, 8·0, and 6·9 respectively, and there seems little doubt that Bishop's results are all far too low owing to an incorrect assumption of the value of n_0.

Yours truly,
E. W. B. Gill.

Merton College, Oxford.

XXIII. *A Determination of the Ionization Curve for the Alpha Rays from Polonium in Mercury Vapour.* By T. S. Taylor, *Ph.D.**

Introduction and Description of Apparatus.

THE investigation, herein described, was undertaken for the purpose of determining the Bragg ionization curve for alpha rays in mercury vapour. Since the vapour-pressure of mercury is very low at ordinary temperatures, it was necessary to design and use a type of apparatus adapted to temperatures as high as 300° to 350° centigrade.

After various attempts to construct a piece of apparatus suitable for the work, the apparatus shown in fig. 1 was finally found to work satisfactorily. In the main, it is merely a modification of the general type of apparatus that has always been used in determining the ionization curve for alpha rays in air and other gases.

The ionization-chamber, shown in the top of the central portion of the diagram, consisted of an insulated iron plate A about 3 centimetres in diameter, and two iron gauzes below it. The iron plate was about 2·5 millimetres above the upper gauze and was joined to the electrometer by means of the connexion that supported it in the tube. The upper iron gauze was joined to a constant potential of 80 volts and the lower one was earthed. The two gauzes were separated and insulated about 2·5 millimetres from each other by means of mica disks. The mica disks were held tightly together by having thin iron disks above and below them which were held together by means of screws extending through the mica disks. These mica disks were of such size as to just slip easily into a glass tube 5·5 centimetres in diameter. The connexions to the two gauzes and the iron disk A were sealed through the glass tube as shown. An earthed iron guard-ring represented by the shaded portion was slipped into the small tube that extended above the main tube and through which the rod supporting A extended. A similar earthed guard-ring was put around the outside of the same tube. These rings were split so as to allow for the expansion when heated. They prevented any leakage over the surface of the glass to the plate A.

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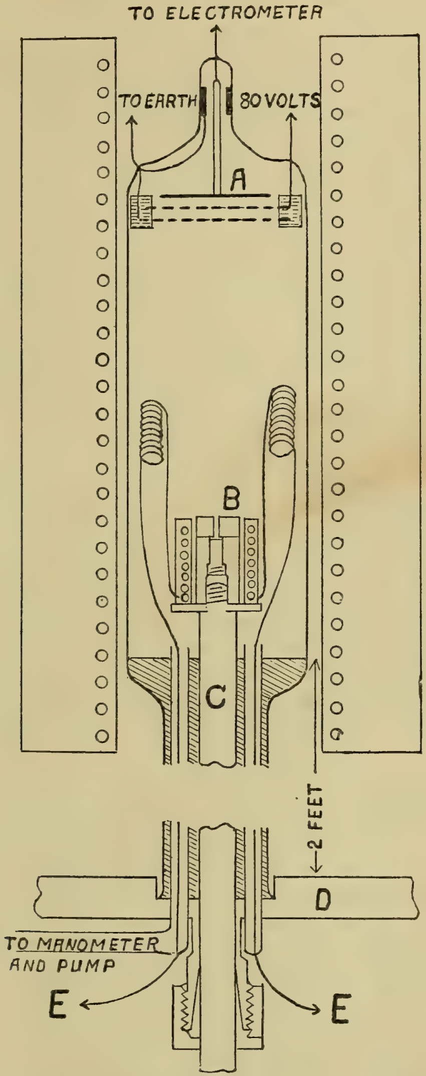
* Communicated by the Author.

Fig. 1.



The polonium was deposited upon the end of a copper plug, and this plug fitted into an iron one B having a small opening about 1 millimetre in diameter and 6 millimetres high over the top of the polonium. This opening gave a small pencil of rays that fell well within the limits of the ionization-chamber. A thin sheet of mica, equivalent to 2 millimetres of air, was placed over the polonium so as to prevent any mercury from coming into direct contact with it and the copper plug upon which the polonium was deposited, in case any should condense in the opening above them. The iron plug B containing the polonium was screwed upon the end of a long iron rod C, 1·5 centimetres in diameter and 100 centimetres long. This rod was turned out carefully so as to be uniform and was fitted snugly into the plate D as a tight piston. This was made tight by packing wool-asbestos in the conical shaped opening at the lower end of the extension of the plate D, and then turning down the nut around the piston as shown in the figure. The lower end of the rod C had a screw of 1 millimetre pitch upon it that passed through a nut supported in a framework extending below the plate D. The framework and nut are not shown in the figure. By turning the nut, the rod C and hence the polonium could be moved toward or away from the ionization-chamber. The exact position of the polonium could be determined by reference to a scale parallel to C and the fraction of a turn that the nut had made. About 12 centimetres from the top of the glass tube, it was drawn down and a smaller tube of 3 centimetres diameter sealed on. This tube extended to the plate D, making a distance of 70 centimetres from the ionization-chamber to the plate D. The glass tube was fastened to the plate D by means of sealing-wax.

A small electric furnace was constructed and placed around the iron plug B, for the purpose of preventing the condensation of any mercury vapour upon the mica over the polonium, and also to assist in maintaining a constant temperature throughout the tube. The wires leading to this furnace were inserted through two glass tubes that were extended through the plate D. These tubes were fastened so as to be air-tight where they extended through D by sealing them in with wax. The lead wire E was sealed directly through the end of one of these tubes. The other tube, besides having the wire leading to the electric furnace sealed through it, was extended to the open manometer and air-pump as indicated in the figure.

The entire upper end of the glass tube containing the ionization-chamber, polonium, &c. was enclosed in a larger electric furnace as indicated in the figure. Alternating current was used in both the large and the small furnace. The ends of the larger furnace were shielded as well as possible by means of asbestos so as to prevent rapid loss of heat.

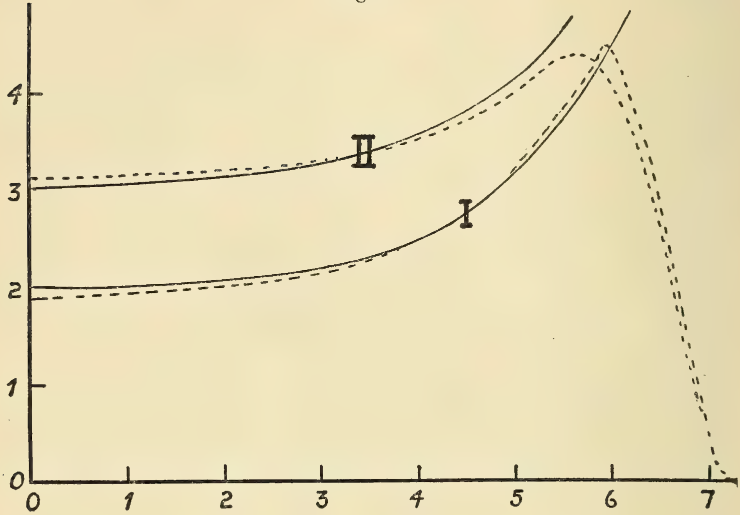
Determination of the Ionization Curve.

By means of a tube similar to the one used but having an opening at the top for the insertion of a thermometer, determinations were made to ascertain the value of the current that must be sent through the small electric furnace surrounding B in order to keep B at a temperature very slightly above that of the other part of the tube. By keeping this slightly warmer, about one-fourth of a degree, it was assured that there would be no condensation of the mercury vapour upon the top of the polonium. In case any should condense it would interfere seriously with the experiment.

The entire apparatus, as described above, was evacuated, and then by means of an open air-manometer a basin of mercury was raised till it rose to the top of one of the glass tubes extending through D. The mercury was then allowed to flow into the apparatus till it filled the tube to within one centimetre of the top of the glass tubes through which the wires leading to the electric furnaces were inserted. The currents were then started in the two furnaces and increased slowly till such values were reached as would raise the temperature to 330 degrees centigrade. The vapour-pressure of mercury at this temperature was 451 millimetres. The alpha particles had a range of 7·30 centimetres in the mercury vapour at the above temperature and pressure. After the temperature had become steady, measurements were taken of the deflexions of the electrometer for the various distances of the polonium from the ionization-chamber. By plotting the deflexions of the electrometer in scale-divisions per minute as ordinates, and the corresponding distances of the polonium from the ionization-chamber as abscissas, a curve similar to the dotted curve II. in fig. 2 (p. 300) was obtained. Several determinations of this curve were made under similar conditions, and the dotted curve II. in fig. 2 was plotted from the entire series of observations. It is seen that the curve does not have nearly such great differences in the values of the ionization at different points along the curve as has been found in other gases and vapours.

The mercury was later removed from the apparatus by means of a small tube extending through D, but not shown in the diagram, and determinations made for the air-ionization curve when the temperature was 330 degrees centigrade and the range of the alpha particles the same in the air as it was in the mercury vapour. The range was made the same by adjusting the pressure by means of the manometer. The dotted curve I. in fig. 2 represents the air curve as determined under these conditions. In plotting both curves corrections were made for the loss of range due to the mica over the polonium.

Fig. 2.



The full-line curves in fig. 2 represent the theoretical curves for air and mercury vapour, respectively, corresponding to the theoretical curve

$$I = \frac{c}{(r-x)^{1/3}}.$$

This is the theoretical curve that has been established by other experiments * for air and other gases and vapours. In this formula I is the ionization, c is a constant depending upon the gas, r is the average range of the particles in the beam, and x is the distance the particle has gone in the gas. The value of r was taken as 7·1 centimetres in this case. It

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* Geiger, Proc. Roy. Soc. Series A, vol. lxxxiii. no. A. 565, p. 505; Taylor, Phil. Mag. April 1911.

is seen that the theoretical curve for mercury vapour agrees fairly well with the experimental one. It seems to vary, however, more from the experimental curve than any of the curves for the other gases and vapours for which it has been tried.

By measuring the areas under the experimental ionization curves, I. and II., and finding the ratio of the area under the air curve to the area under the mercury vapour curve, the ratio of the amount of energy required to produce an ion in mercury vapour to that required to produce an ion in air was found to be 0·72. That is, it requires only 0·72 as much energy to produce an ion in mercury vapour as it does in air.

In conclusion I wish to express my thanks to Professor A. P. Carman for furnishing me the facilities by means of which it was made possible to carry out this research.

Results.

1. The ionization curve for the alpha particles from polonium has been determined in mercury vapour, and found to be of the general type as has been found for other gases and vapours*.

2. The alpha particle loses 0·72 as much energy in producing an ion in mercury vapour as it does in air.

Physics Buildings,
Urbana, Illinois,
June 6, 1912.

XXIV. *Coloured Photometry.*

By Lord Rayleigh, *O.M., F.R.S.*†

In his recent paper on the Photometry of Lights of Different Colours ‡ Mr. H. Ives remarks:—"No satisfactory theory of the action of the flicker photometer can be said to exist. What does it actually measure? We may assume the existence of a 'luminosity sense' distinct from the colour sense. . . . . . If, for instance, there exists a physiological process called into action both by coloured and uncoloured light, a measure of this would be a measure of a common property."

Very many years ago it occurred to me that the adjustment of the iris afforded just such a "physiological process"*. The iris contracts when the eye is exposed to a bright red or to a bright green light. There must therefore be some relative brightness of the two lights which tends *equally* to close the iris, and this may afford the measure required. The flicker adjustment is complete when the iris has no tendency to alter under the alternating illumination.

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* *Loc. cit.*

† Communicated by the Author.

‡ Phil. Mag. vol. xxiv. p. 178.

This question was brought home to me very forcibly, when in 1875 I fitted the whole area of the window of a small room with revolving sectors after the manner of Talbot. The intention was to observe, more conveniently than when the eye is at a small hole, the movements of vibrating bodies. The apparatus served this purpose well enough; but incidentally I was much struck with the remarkably disagreeable and even painful sensations experienced when at the beginning or end of operations the slits were revolving slowly so as to generate flashes at the rate of perhaps 3 or 4 per second. I soon learned in self-defence to keep my eyes closed during this phase; and I attributed the discomfort to a vain attempt on the part of the iris to adjust itself to fluctuating conditions.

It is clear, I think, that we have here a common element in variously coloured lights, such as might serve as the basis of coloured photometry. I suppose that there would be no particular difficulty in observing the movements of an iris, and I would suggest that experiments be undertaken to ascertain whether in fact the flicker match coincides with quiescence of the iris. Should this prove to be the case, the view suggested would be amply confirmed; otherwise, it would be necessary to turn to some of the other possibilities discussed by Mr. Ives.

XXV. *On Contact Difference of Potential, and the Action of Ultra-Violet Light.* *By* Prof. A. Anderson, *M.A.*, *and* H. N. Morrison, *B.Sc.*†

THE contact difference of potential of two metals depends on the state of the surfaces of the metals. The effect of making the surface of a metal bright and clean is to render it more electropositive to other metals, and the magnitude of the effect is different for different metals. The following is the result of a careful experiment on this point. The numbers give the contact difference in volts relative to a plate of uncleaned copper. Judged by their appearance, the uncleaned copper and zinc plates must have lain in the laboratory for many years.

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* If my memory serves me, I have since read somewhere a similar suggestion, perhaps in Helmholtz.

† Communicated by the Authors.

	Volts.
Freshly cleaned zinc	0·826
Uncleaned zinc	0·466
Freshly cleaned copper	0·060
Uncleaned copper	0·000

The effect of cleaning was the same in the case of both copper and zinc, but much more marked for the latter. With lapse of time the surface of a metal, whether from oxidation or from some other cause, changes so as to make the metal more electronegative. To get the maximum contact difference between two metals, the electropositive one must be quite clean, and the electronegative one must have as much of the opposite quality as possible. Thus, according to the above results, while the contact difference between freshly cleaned zinc and freshly cleaned copper was 0·766 volt, that between freshly cleaned zinc and uncleaned copper was 0·826 volt. It is probable that the surface of a metal exposed to the air approximates to a state in which the potential of the metal is equal to that of the air in contact with it.

It is perhaps not too much to assume that, whatever be the cause of contact difference of potential, it has its seat in the surface and not in the interior of the metal. Possibly, therefore, some light may be thrown on it by other electrical effects at the surface of metals. One such effect is that of ultra-violet light, and the experiment herein described was devised with the object of obtaining measurements of the contact difference of potential between zinc and copper while and after the former was exposed to rays of ultra-violet light. The result of the experiment was to show that, with a powerful source of ultra-violet light, there is a decided electronegative increase, which disappears slowly when the source is removed.

To understand what, on the electron theory, takes place when a metal becomes more or less electropositive, let us suppose we have two metals, A and B, in contact at the same temperature and connected to earth, that is kept at the same constant potential. From considerations bearing on the Peltier effect at the junction of two metals, the number of free electrons per unit volume in A will differ very slightly from the number per unit volume in B. We will suppose these numbers equal. If, now, by any means A be made more electropositive, there will be a flow of negative electrons from A to B and thence to earth ; and, in fact, A will receive a positive charge. But the number of free electrons per unit volume in A is still equal to that in B; and, consequently, A must have lost some of its bound electrons. Hence, when the number of bound electrons in a metal increases it becomes more electronegative, and when the number decreases it becomes more electropositive. Different metals in contact have the same number of free electrons per unit volume, but the number of bound electrons varies, those metals which are more electronegative having the greater number.

Zinc, being electropositive to copper, has less bound electrons per unit volume than copper when both are at the same potential. This may be due to a difference in the atoms of the two metals, on account of which the bound electrons are more strongly held in the copper than in the zinc ; but this does not imply that the positive atomic charges are greater in the copper. It can be accounted for by supposing a difference in the size, shape, or structure of the positive atomic charges in different metals, just as the electric field in the neighbourhood of a charged conductor depends not only on its charge but also on its capacity. Indeed, we might speak of the electric capacity of an atom with perhaps as much propriety as we speak of its thermal capacity.

It is clear that in every case where a metal is rendered more electropositive, work must be done on it, whether by mechanical action or by some other agency; and, when it becomes more electronegative, it does work at the expense of its own energy,

Here we may mention a difficulty referred to in a paper in the 'Proceedings' of the Physical Society, vol. xxiv. part ii. p. 105. It has to do with the energetics of a copper-zinc uranium-oxide cell. Two plates, one of copper and the other of zinc, connected by a wire and immersed in ionized air form the cell. There will be a field of force producing a current in the air between the plates, which we may suppose to consist in the passage of electrons from the copper to the zinc through the air between. If one effect of this transference of electrons be to make the copper more, and the zinc less, electropositive, the zinc will receive a negative charge and the copper a positive one ; and one effect will be a decrease of the contact difference of potential. Whether this be so or not is a question to be settled by experiment, which, however, presents some difficulty owing to the smallness of the currents and to the fact that the contact difference decreases from other causes with the lapse of time. But it is quite easy to show that, if a current of negative electricity be sent from a battery of cells from a copper to a zinc electrode in ionized air, the copper becomes more, and the zinc less, electropositive.

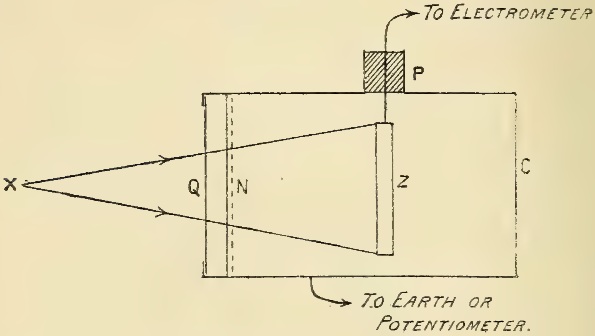
The difficulty in the case of the uranium-oxide cell was that, in applying Helmholtz's theory, it was found that an amount of work, presumably at the surfaces of the metals, must be accounted for. In the light of the above remarks, it seems clear that this work is the total work done in rendering the copper more, and the zinc less, electropositive. In the case of the cell described in the paper it was found that the amount of this work per unit quantity of electricity was such as to produce a back electromotive force of 0·276 volt. Let us assume that the only electrons taking part in the cell action are bound electrons set free at the surface of the copper, which again become bound electrons at the surface of the zinc. The work done per unit of electricity is, therefore, $\cdot 276 \times 10^8$ erg. But one unit of negative electricity contains $6\cdot 4 \times 10^{19}$ electrons. The work done per electron is, therefore,

$$\frac{\cdot 276 \times 10^8}{6\cdot 4 \times 10^{19}} = \cdot 43 \times 10^{-12} \text{ erg.}$$

On the above assumption, this is the difference between the work necessary to take an electron out of an atom of copper and the work necessary to take an electron out of an atom of zinc. Various estimates have been made of the amount of energy necessary to ionize a molecule of a gas, and H. A. Wilson and Townsend obtained by experiment a value for this energy of about 3×10^{-12} erg in the case of a molecule of air. Campbell ('Modern Electrical Theory,' p. 222) states that the energy required to drag an electron out of an atom probably lies between 130×10^{-12} and $1\cdot 3 \times 10^{-12}$ erg.

To return to the experiment with ultra-violet light, the method used will be clear from fig. 1 (p. 306). C is a cylindrical copper vessel which can either be earthed or connected to a potentiometer, according as the deflexion or nul method is used in measuring the contact difference. Z is a zinc plate connected to one pair of quadrants of the electrometer by means of a zinc wire which passes through an amber plug P. The vessel is closed by a quartz plate Q in contact with which and in connexion with the cylinder is a network of copper wires N. *X* is the source of light, a quartz-glass mercury vapour lamp. Inside the cylinder was placed a shallow paraffin dish containing uranium oxide. If everything is at first earthed, and then the quadrants in connexion with Z insulated, the deflexion of the electrometer-needle will give the contact difference of potential of the zinc plate and copper vessel. The object of the experiment is to find the change in the deflexion produced by the ultra-violet light. It must be observed that there are two effects on the needle caused by the action of the light. The first is the loss of electrons by Z, which means the communication to it of a positive charge. The second is the increase or decrease of the contact difference of potential which results in the communication of a negative or positive charge to Z.

Fig. 1.



On account of these interfering effects, it was found more satisfactory to first expose the zinc plate for a certain time to the source, and then immediately afterwards to measure the contact difference. It must be remembered that, as one face only of the zinc plate was exposed, and as the other face was not cleaned, the result has no importance from a quantitative point of view. In one experiment the zinc plate was exposed for 30 minutes. The contact-difference before exposure was ·45 volt, after exposure it was ·27 volt. It then gradually rose and nearly attained its initial value in nine days, after which it fell very slowly. It thus appears that in the case of zinc the effect, although lasting for a very appreciable time, is temporary. An experiment, in which a plate of aluminium was substituted for the zinc, showed a fall from 1·01 volt to ·37 volt, with a gradual rise in three days to ·48 volt, after which it remained practically steady for several days, and was not measured afterwards. No doubt it will begin to diminish in accordance with the very rapid decrease of the contact-difference of aluminium and copper observed in ordinary cases. It is rather remarkable that, if the above theory be correct, the more electropositive a metal is the less the number of bound electrons in the atom, the effect of ultra-violet light should be to make a metal temporarily more electronegative, as one known effect is to expel electrons from the surface. It would seem as if it not only projected electrons out of the surface, but projected them into the atoms as well. It would be interesting to investigate whether, by charging the metal positively and thus preventing the expulsion of electrons, the decrease in contact-difference would also be prevented.

A rather striking experiment which, no doubt, is connected with the above subject is the following. If a plate of zinc or aluminium, or indeed of any metal—but the effect is more marked in the case of zinc and aluminium—be exposed to ultra-violet light for a short time, the light passing through a geometrically shaped aperture in a screen, a distinct pattern will be observed on the metal of the same shape as the aperture. It was observed in the case of copper, brass, silver, and platinum.

XXVI. *On Magnetic Rays.* *By* Louis T. More, *Professor of Physics, and* Edward G. Rieman, *M.A., Hanna Fellow in Physics, University of Cincinnati*[*].

PROFESSOR RIGHI has applied the term "magnetic rays" to certain phenomena which occur when an electric current in rarefied air is influenced by a strong magnetic field. It has, of course, been known for a long time that a magnetic field altered the path and appearance of such currents, but it was generally believed that all the effects noted were due to an orbital motion given to the cathode rays by the magnetic force. Professor Righi has investigated the subject most elaborately and has come to the conclusion that the action of the magnetic field may give rise also to a new and special kind of rays. His results have appeared in numerous articles[†], which have lately been made more accessible by being revised and collected in a book. He has not only given his own results but he has also prefaced them by an account of the work of his predecessors.

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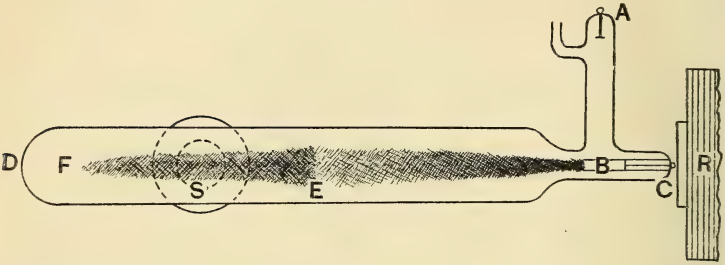
[*] Communicated by the Authors.

[†] *Mem. della R. Accad. dell' Ist. Bologna*, 1908 and 1909. *Le Radium* 1910.

The brief abstract of the results and theory of Professor Righi which pertain to the subject of the present article is taken from a German translation of his book, published by Barth under the title *Strahlende Materie und Magnetische Strahlen.*

The apparatus best suited to show the magnetic rays consists of a Geissler tube about a metre long and five centimetres in diameter (fig. 1). The anode is either an aluminium rod or disk placed in a branch tube, A. The cathode is situated at one end, C, in a somewhat narrower extension of the main tube; it usually takes the form of a small aluminium disk, enclosed in a little glass tube that extends beyond the disk. The current is supplied by a high tension battery, an electrostatic machine, or an induction-coil. R is a large electromagnet with the iron core removed, placed so that its axis coincides with the axis of the tube. The necessary field-strength varies from 500 to 2000 units at a distance of a centimetre and a half from the end of the spool, although most of the results are obtained near the lower limit.

Fig. 1.



When the field magnet, R, is not excited, the ordinary discharge takes place between the anode and cathode, and the tube BD remains dark; but if, while the discharge is passing, the magnet is excited to give a certain critical intensity of field depending on the size of the tube, the pressure of the gas, and the potential of the cathode, the whole tube is suddenly filled with a glow discharge, represented by the column BEF. The nature of this glow discharge can best be determined by an auxiliary magnet, S, held near the tube and with its axis horizontal but perpendicular to that of the field magnet R.

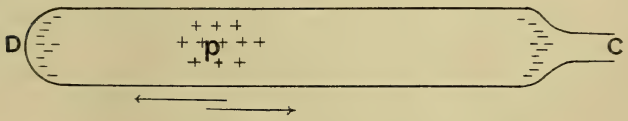
While the magnetic field is weak, the two bluish-violet bright bands, separated by the negative dark spaces, are seen in the tube surrounding the cathode, and the pink anode column fills in the side tube. As the magnetic field increases the second negative bright band gradually lengthens and creeps into the large tube, until at the critical intensity the whole tube is filled suddenly with a glow discharge. If the magnetic field be still further increased, the discharge attains a maximum length and definition, and then diminishes in length. From B to E the light is similar in colour to the cathode rays in air, and from E to F it is reddish or more like a positive column. At E, the two parts of the column are separated by a rather dark space.

If the magnet S is held with its axis horizontal and with its pole near the portion of the tube between B and E, the rays bend in the arc of a horizontal curve. They bend toward the pole of the magnet, if this pole is of opposite sign to the nearer pole of the magnet R; and they bend directly away from S if the poles are similar. On the other hand, an electrical field produces no effect on these rays. That is, the rays act as if they were composed of a moving stream of electrically neutral particles which are at the same time elementary magnets. Because of these actions, Professor Righi has applied the term "magnetic rays" to this part of the column.

The rest of the column EF has its origin in these magnetic rays and will be called the induced ray. If S is held horizontally and with one pole near the induced ray, the column bends vertically like the positive column in a Geissler tube. The curvature of the ray is the same as would be produced by a similar magnetic field acting on a current of positively charged particles moving from E to F. The action is seen more clearly if electrostatic discharges are prevented by enclosing the tube in an earthed metallic screen of copper gauze.

When the conditions are such that a very long induced column is formed, a different effect is shown by the magnet S. As it is moved along the tube a point is reached, indicated by *p* in fig. 2, where the light splits into two helically curved bands. Then as the magnet is moved toward E or toward F, the bending of the column is opposite in curvature; if it bends up on one side, it bends down on the other.

Fig. 2.



The direction in all cases is as if there were a virtual anode at *p*, due to a piling up of positively charged ions, and a positive current flowing toward each of the two ends, D and C, as shown by the arrows. The discharge can also be shown to be intermittent either by viewing it in a rotating mirror or by the fact that when it is intense it gives out a high-pitched musical note.

Professor Righi explains all these actions by assuming the magnetic rays to be due to what he calls planetary doublets (Doppelsterne) which consist each of a gas or metal ion, positively charged, and an electron revolving about it in an orbit. The bond of electrical attraction between them, due to their distance apart, is of such a magnitude that they may be classed as intermediate between a neutral atom and an atom entirely dissociated into an ion and an electron. He supposes that in a Geissler tube, and especially near the region of the second cathode bright space where there are many positive ions and electrons moving in opposite directions, neutral systems of particles exist in addition to the free, dissociated ions and electrons. These systems are of two kinds: neutral atoms which are formed when an electron with the proper speed comes so close to an ion as to be captured by it and held in a permanent chemical bond, and doublets where the speed of an electron is such that, while it is captured by the ion, they do not coalesce. The result in the second case is that the electron revolves about the ion as a satellite and forms an electrically neutral system, which is not very stable. Ordinarily these doublets are comparatively few in number and so short lived as not to be detected. Such a doublet, while it persists, should act like a magnetic shell, since the motion of the electron makes it equivalent to a small closed electric current.

As the presence of a magnetic field causes these doublets to persist, it must be shown that the magnetic force exerts a mechanical force on the system tending to increase its stability. The simple case of an electron rotating about a positive ion in a plane perpendicular to a uniform magnetic field has been discussed by Professor Righi, and he has shown that there is a resultant electromagnetic force on the electron in the plane of rotation and radial: either towards or away from the centre, depending on the direction of rotation of the electron. Consequently, all those doublets having a rotatory motion in one sense will have their stability increased by a given uniform magnetic field, and those whose motion is in the opposite sense will be destroyed. If, however, the magnetic field be not uniform, then the resulting electromagnetic force is not in the plane of rotation but has a small translational component along the axis of rotation. The direction of this component is such that a doublet whose stability is increased by the magnetic field moves toward regions of lower magnetic intensity.

This hypothesis, if accepted, would account for the extension of the luminous column from the region near the cathode out into the large tube, since the stability of the doublets is increased and a translational motion given to them by the non-uniform field created by the magnet R. It also explains why this column bends towards the magnet S or away from it according as the unlike or like poles of the two magnets are nearest each other. As these doublets move out into the tube, collisions with the gas in the tube, together with the diminishing electromagnetic force, cause their destruction, which is marked by the position E. The freed electrons cause dissociation in the gas, and the limit of range of the positive ions is marked by the region *p* which, on account of the accumulation of positive electricity there, acts like a virtual anode. The free electrons tend to go past the point *p* and, in fact, usually travel to the far end of the tube for two reasons: the range of electrons is in general greater than that of positive ions, and the cathode exercises a repulsive force on the electron and an attractive force on the positive ion. The effect of this action is a Geissler tube discharge in the ionized gas toward both ends of the tube from this virtual anode. The oppositely directed currents in the induced column are indicated by the reversed curvature of the rays around the pole of S on the two sides of *p*.

Such, in brief, is Professor Righi's hypothesis to account for the action of a magnetic field on the current in a vacuum tube. It is simple, plausible, and accounts for most of the observed phenomena. Still there are some facts brought out in our experiments which indicate that the actions occurring are rather more complex and obscure. Apparently, Professor Righi limited his work to experiments with air; we find that other gases give rise to quite distinctive effects.

Our apparatus was, for the most part, similar to that of Professor Righi. Some of the tubes were obtained from Herrn Richard Müller-Uri and were made according to Professor Righi's specifications; others were made in our laboratory. They were of various sizes; in some the anode was placed in a side tube, and in others the narrow portion of the tube was made long and pushed into the core of the field magnet. The anode was, in the latter tubes, inside the magnet and the cathode just in front of the pole; the magnetic rays then proceeded from the back of the cathode. The current was obtained from an induction-coil. The magnet-coil was a large one, and the space in the core left by the tube was filled with soft-iron wires to increase the field-strength. The magnet was capable of developing a field much in excess of the requirements, since with a maximum current it became so intense as to destroy the rays; an effect noted by Professor Righi.

The tube was filled with air which had been thoroughly dried by passing it through sulphuric acid and phosphorus pentoxide. The first observations were made when the rays were not subjected to a magnetic field. As the pressure was reduced, the appearance of the current passed through the usual stages of the Geissler tube discharge. When a pressure of 0·2 mm. was reached, the two layers of negative glow and the cathode dark spaces were well defined in the little glass tube surrounding the cathode. Under such conditions Professor Righi observed that the large part of the tube remained dark, but our experience was that almost the whole tube was filled with pale bluish light. This discharge was evidently a mixture of cathode rays and an induced electrostatic discharge from the walls of the tube. The tube was not covered with a conducting earthed screen, and a finger touched to the glass produced a characteristic brush discharge. The electrostatic effect could be entirely eliminated by slipping over the tube an earthed screen of copper gauze, but even under those conditions some glow persisted in the tube. The trial was then made with the field magnet excited. As soon as the discharge was influenced by the magnetic field, the diffuse light in the large tube began to condense and contract into a column of light along the axis of the tube. Suddenly, when a critical pressure and magnetic field were reached, the appearance completely changed; the induced electrostatic discharge at the far end of the tube disappeared, and in the centre of a faint and diffuse cathode discharge the true magnetic rays appeared as a sharply defined cone of blue light stretching along the axis of the tube and extending into the large part of the tube about one-fourth its length. These magnetic rays bent toward an auxiliary magnet if the poles of it and the field magnet nearest each other were opposite in sign, and were repelled if the poles were alike. At the end of the magnetic rays appeared the induced column EF (fig. 1). This light was rather reddish in colour, and showed the characteristic opposite curvature when the auxiliary magnet was moved along it, as indicated in fig. 2. Many observations were made of these phenomena, and both the pressure and magnetic field were varied so as to get all possible combinations. In general, the rays were more sensitive to changes of pressure than to variations in the magnetic intensity. For a given pressure, the magnetic field could be changed within wide limits without any other apparent effect than to increase or diminish somewhat the intensity and length of the rays; but with a given field, changes of pressure would soon destroy the rays altogether. In our apparatus the magnetic rays appeared quite suddenly at what may be called the critical pressure. This pressure was approximately 0·03 cm. As the current of the magnet was increased the rays gradually grew longer and having attained a maximum began to shorten until, with a sufficiently intense field, they suddenly ceased. The lowest pressure in which the rays could exist was about 0·006 cm.; and, in general, as the pressure decreases the strength of the field must be increased.

The tube was next filled with illuminating gas, thoroughly dried. This gas is a natural gas obtained from wells and of unknown but probably complex composition. When the electric discharge was observed without a magnetic field, the cathode rays were less dense and of a paler blue than in air. The action of the magnetic field showed a decided difference. The magnetic field, apparently, was unable to contract the diffuse cathode rays into a well defined magnetic ray column. Even when a field was used sufficiently intense to destroy the action in air, the diffuse light filled nearly half the tube; the axial portion was slightly brighter, somewhat more blue in colour and extended only a short distance into the large tube, but no well defined column could be observed. This inner core showed the characteristic deflexions of magnetic rays when an auxiliary magnet was used. But the induced column of light at the end of the magnetic ray was lacking and could not be produced with any pressure and field. That the gas used in the tube should have such an influence on the nature of the magnetic rays is most difficult to explain by Professor Righi's hypothesis.

Various simple gases were used successively. Hydrogen, oxygen, nitrogen, and carbon-dioxide gases were prepared in as pure a state as possible and were thoroughly dried before being admitted to the tube, and the tube was filled and emptied many times to get rid of other gases, especially air. In no case, with any of these simple gases, could the discharge characteristic in air be obtained. The pressure and magnetic field were varied between wide ranges, from the limit where a simple glow discharge, without negative dark spaces, passed between the anode and cathode, to so great a vacuum that the induction-coil could not produce a luminous discharge at all. The appearance in each of the gases most nearly approaching that in air was a more or less diffuse cathode glow filling about half the large part of the tube with a core of magnetic rays short and sharply conical in shape, lying along its axis. The induced column at the end of these rays with a virtual anode and a reversed curvature was never obtained. If any of these gases were mixed with air, either by admitting a little air into the tube or by not removing all of it, then all the phenomena characteristic of the discharge in air were readily obtained. This fact made it certain that the gases were pure when the phenomena were not obtained.

Trials were then made with mixtures of the gases. Neither hydrogen or oxygen mixed with carbon dioxide in any proportion gave the effect. The magnetic rays were somewhat longer and larger, and there appeared occasionally a small induced column, but it always bent, in an auxiliary magnetic field, in the same direction throughout all its length, and the curvature indicated a positive current from the end of the magnetic ray column to the far end of the tube. There was no virtual anode in it with the positive current discharging in both directions as shown in fig. 2.

Mixture of nitrogen and carbon dioxide.—This mixture gave all the effects of air; both the magnetic rays and the induced column with a virtual anode were observed at the same pressures as for air. The discharge was rather less intense, but the magnetic field was able to condense all the diffuse glow into an axial column.

Mixture of nitrogen and oxygen.—The appearance was exactly that of air.

Mixture of nitrogen and hydrogen.—This mixture acted like air but much less certainly. The best proportion of gases was about six parts of nitrogen to one of hydrogen, If the proportionate part of nitrogen was much less, the induced column could not be produced.

We have been able to repeat satisfactorily the most important phenomena discovered by Professor Righi when a magnetic field acts on the cathode rays in a tube containing air; and we have, in addition, found that the nature of the gas has an important influence on this action. While it is not possible to state fully and exactly what these differences are and what their cause may be, yet our observations point to the conclusion that the magnetic rays are much more easily produced in air and artificial mixtures of nitrogen and oxygen than in the other mixtures we tried ; and they, in turn, are more sensitive to the influence of the field than simple gases, including the chemical compound carbon dioxide.

As regards what has been called the induced column, that is, the glow proceeding from the end of the magnetic rays which acts as if it were a current of charged ions moving in opposite directions from a virtual anode situated at a point in the column, we could obtain it in a well developed form only for air. While we also observed it with other mixtures containing nitrogen, the characteristic phenomena were less certain ; in other mixtures and in simple gases it was absent. This seems to be correct, because if either pure nitrogen or oxygen were in the tube and a little of the other gas introduced, the induced column immediately declared itself.

These results are difficult to account for by Professor Righi's hypothesis. If the magnetic rays consist of a stream of doublets, each composed of a centre of a positively charged gas-ion, or metal-ion detached from the cathode, why should the doublets form more readily in a medium containing gas-ions of one gas rather than another, and especially when two gases not chemically combined are present.

Again, Professor Righi supposes that those doublets, which are made more stable by the action of a magnetic field and are driven by it toward regions of less intensity, have their stability decreased as their distance from the magnet increases. These doublets are finally destroyed by collisions, and their dissociated parts move on and ionize the gas. The range of these particles is shown by an excess of free positive electricity at a certain place in the tube which he calls a virtual anode. It is difficult to see why the existence of this virtual anode should depend on the gas. It might be claimed that for a light ion like hydrogen the virtual anode would be too near one end of the column, and for a heavier ion like nitrogen or oxygen too near the other end to make the reversed bending on the two sides of this anode evident. But this can hardly be the explanation because, while the column should then curve as a whole in one direction, yet the directions should be opposite for the columns of the two gases. This is not the case, for it always curved the same way for all gases and mixtures when the column was present, and the virtual anode could not be located.

Lastly, the hypothesis requires that a doublet be driven from an intense to a weaker part of the field, and this is in agreement with the fact that the magnetic ray curves toward an auxiliary magnet when the two nearest poles of it and the field magnet are unlike in sign, and is repelled when these poles are of like sign. Now, the magnetic field in these experiments is produced by a magnet placed at one end of the tube and the magnetic lines of force diverge in the tube. The fall of magnetic potential is also least rapid along the lines which lie near the axis of the tube. It would seem as if the magnetic rays, when the auxiliary magnet is not used, should be a diverging cone of light. Yet the most noticeable action of the magnetic field is to condense the light near the axis of the tube. And the stronger the field is made, the more sharply converging the cone of light becomes and the more contracted to the axial part of the tube.

These experiments should not be regarded as other than very incomplete, since the phenomena appear to be quite complicated. The attempt is being made to increase the discharge without unduly increasing the potential and to study the action of other gases and the state of the gas in different parts of the tube.

University of Cincinnati,
April, 1912.

XXVII. *Preliminary Note on the Electron Atmospheres of Metals.*

By R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University*[*].

THERE has been a good deal of controversy recently as to whether air at atmospheric pressure will carry a current of electricity, when the potential between the electrodes is less than what is known as the critical potential (something over 300 volts). Earhart, in a paper published in 1901 (Phil. Mag. [6] i. p. 147), described experiments which appeared to show that a discharge might occur with as low a potential as 32 volts, the gap between the electrodes being of the order of magnitude of the wave-length of light. This result was called into question by Almy, who worked with very small platinum beads as electrodes, and failed to obtain any evidence of discharge at voltages below 300. During the progress of the work about to be described a paper appeared in the Phil. Mag. by Anderson and Morrison (May 1912) which gives further evidence that currents may flow across minute air-gaps at very low voltages, though no data are given as to the precautions taken to exclude the presence of foreign matter between the plates, or how the exact distance between them was determined.

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[*] Communicated by the Author.

The experiments which I am about to describe were the outgrowth of a piece of work on the electrical properties of very long heat-waves (112 μ obtained by focal isolation) which has occupied a portion of my time during the past winter. Having found that quartz plates thickly coated with very fine copper dust, or with closely packed droplets of mercury, were perfectly transparent to the heat-waves, opacity commencing only when the size of the metal particles exceeded one quarter of the wave-length, I commenced experiments with silver films deposited on quartz and ruled with a diamond point into a microscopic checker-board. The rulings were made for me by Dr. J. A. Anderson, who has worked out the technique of ruling thin metal films to such a point that clean cuts, quite through the metal, of a width certainly no greater and probably less than the wave-length of ultra-violet light are possible. The great trouble in making very close rulings on thin metal films is the tearing of the metal, which causes the cuts to run together. Successful rulings occur only when a natural edge of the diamond is used and the edge set accurately parallel to the direction of the cut. The silver was deposited on thin plates of quartz, the thickness being what is usually described as "half-silvered," and the plates were found to be absolutely opaque to the heat-waves. A cross ruling was then made breaking the film up into squares measuring about 0·1 of a wave-length on a side, *i. e.* 0·011 mm. From the results of the experiments with the mercury droplets I expected to find the waves freely transmitted, but the ruled film was found to be quite as opaque as before. The electrical resistance of the film was then compared with that of an unruled one with a box-bridge and galvanometer, and found to be practically the same. This result seemed most astonishing, for the cuts when examined with a 1/12 inch oil-immersion objective were found to be clear through the film, there being no conducting bridges across the gaps.

A second film was now deposited on a glass plate, and wiped off with the exception of a strip about 3 mm. in width, terminating at each end in a larger patch of silver, against which the electrodes of silver-leaf rolled into soft balls were clamped. About 20 diamond cuts were made across the narrow strip, and its resistance measured. Before the cuts were made the resistance was 10 ohms, which was increased to only 13 ohms by the cuts. I feel confident that the diamond removed all of the metal from the cuts, for they appeared as brilliantly illuminated under the microscope as the clear glass from which all of the silver had been removed.

Photographs of the rulings were made with a 1/12 inch oil-immersion objective, and the width of the cut determined by comparing it with the distance between the cuts, the measurements being made with a dividing engine. In the majority of cases the width turned out to be no greater than the diffraction maximum yielded by the objective, and in some cases it was probably less, the cuts appearing slightly greyish, as would be the case if the width was less than the resolving power of the objective. This makes the order of magnitude about equal to the wave-length of ultra-violet light, say 0·0003 mm. Photographs of the rulings will be published in connexion with the work on heat-waves.

A number of strips of silver were prepared, each one cut across by 20 strokes of the diamond, and the resistances measured by applying soft pads of silver-leaf as electrodes so as to include, or not include, the cross-ruled portion. The increase in the resistance was found to be very variable, for in some cases the original resistance of about 10 ohms was raised to three or four hundred, and in others to 15 or less. With cuts somewhat wider, say two wave-lengths, no trace of conduction could be found, and it seems probable that the great variation can be safely attributed to slight differences in the widths of the cuts, the differences being too small to be shown by the microscope. The voltage applied was that of one dry cell, and by means of a potentiometer it was found that conduction occurred with potentials as low as 0·001 of a volt. Covering the ruled portion with a drop of oil did not alter the resistance, though this is a point that has not been very thoroughly investigated.

It appeared to me possible that the conductivity at these very low voltages might be ascribed to the extent of the opposed surfaces. In all previous work the electrodes have been either spherical or "point and plane," and when brought close together give us what amounts to two opposed points, on account of minute irregularities on the surfaces. If this explanation is the true one conductivity at greater distances should be obtained in the case of two opposed planes.

It is obviously out of the question to use metal plates as ordinarily prepared for electrical experiments, and, as I shall show presently, even gold films deposited on optical flats by cathode discharge are scarcely suitable on account of minute conducting projections. Soft metals cannot be used, for if they are brought in contact there is the possibility of microscopic elevations being raised when they are separated. I accordingly commenced observations with the small optical flats of polished speculum metal, which is glass hard. The surfaces were known to be true planes to within 1/20 of a wave-length, and they were highly polished and free from scratches. Two of these flats were placed in contact, no pressure being applied, and it was found that, so far as ordinary measurements would show, they were in metallic contact. The upper plate slid about easily over the lower with little friction, showing that they were separated by an air-film, and from what we know about the behaviour of true flats brought together under these conditions, we may be certain that the actual distance between them is certainly 8 or 10 wave-lengths. Optical tests showed that the plates rounded off a trifle at the edge, the surface of the outer zone being a trifle convex, which excludes the possibility of true metallic contact occurring at some point at the edge. The speculum plates were now separated by two very fine quartz fibres, about 5 wave-lengths in diameter, as measured with the microscope, and again conductivity was observed, a current of several milliamperes being observed with an applied potential of one volt. The current increased rapidly and very steadily with the application of pressure, returning to exactly its original value as the pressure was removed. Fine sulphur dust was then allowed to settle from an air suspension upon one of the plates and the other plate then laid carefully upon it. Again conduction was observed. Metallic contact at any point was out of the question in this case. There was, however, the possibility that a conducting sulphide was formed, and consequently finely powdered quartz was substituted which gave similar results.

It was impossible, however, to measure the exact distance between the plates under these circumstances, or be quite sure that the presence of the material used to keep the plates at a fixed distance was without influence. Fused quartz is known to be one of the best insulators which we have, and yet a film of adsorbed moisture might be responsible for the conductivity under the conditions of the experiment. I find it difficult to believe, however, that currents of the magnitude obtained, in some cases amounting to a considerable fraction of an ampere, can be carried in this way.

The ideal method is to exclude all material, and work under conditions which enable the exact distance between the plates to be determined. I accordingly used as opposed electrodes the half-silvered films of a Fabry and Perot interferometer. These can be adjusted to absolute parallelism by optical methods, and the exact distance between the metallic surfaces can be determined by placing a white light behind them and counting the number of interference bands which appear in the spectrum of the transmitted light between two lines of known wave-length. The interferometer plates were half-silvered by the formaldehyde process, which gives the most uniform semitransparent films, and were adjusted to parallelism with the soda flame, circular fringes appearing by transmitted light, the diameter of the central circle remaining fixed as the eye is moved about. The plates were mounted in the instrument a little to one side of one another, so that the silver-leaf electrodes could be brought into light contact with the silver films. One dry cell was used with a milliammeter and the plates were gradually approached. In every case a sudden large deflexion of the milliammeter showed that metallic contact had occurred when the plates were still separated by a distance amounting to thirty or forty wave-lengths. It is apparently impossible to obtain silver films free from projecting metallic points, which bridge over the gap which separates them. I imagine that minute matter in suspension or particles of reduced silver settle on the film, and are not removed by the washing process. It seemed, however, as if a cathode deposit of gold thrown down in a vacuum would be free from these objections. Semitransparent films of beautiful quality were deposited on the interferometer plates and the experiment repeated. The same thing happened as before. After repeated trials, using great precautions to remove all dust particles from the glass surfaces, I finally obtained a pair of films which gave a small deflexion of the milliammeter when separated by a distance of 28 wave-lengths. The fringes were still circular, or rather the entire surface of the interferometer plate appeared uniformly illuminated. On gradually approaching the plates the current increased with beautiful regularity, but suddenly when the plates were still over 15 wave-lengths apart a large deflexion was suddenly obtained, showing that metallic contact had occurred. As the plates were still further approached the fringes straightened out and crowded into the field, showing that there was something between the plates which caused a departure from parallelism. I have made repeated trials with gilded plates, but on only two occasions have I succeeded in getting the true effect before metallic contact occurred at some point. It is impossible to polish the films without making them much worse than before.

What is required is a semitransparent film with an optical surface equivalent to that of a speculum plate. It is possible that by using a plate of gold which has never been previously used as a cathode, a suitable film may be procured, for it seems possible that the surface may be rendered spongy by disintegration, resulting in the projection of microscopic particles of gold against the film.

Very good results were obtained by gilding the convex surface of a plano-convex quartz lens of six-foot focus. The central zone of the lens was protected from the deposit by a circular disk of metal 5 mm. in diameter. An electrode of silver-leaf was attached to the gold film at the edge of the lens, which was then laid carefully upon a flat of speculum metal. The centre of the system of Newton's rings observed with white light was brought to the centre of the ungilded circular patch by placing a small weight at the proper point on the lens which gave it the requisite tilt. Even at the centre of the system the interference colour was very pale, showing that the air-film was several wave-lengths in thickness at the so-called point of contact. By applying pressure it was ascertained that the edge of the zone at which the gilded surface commenced was about 8 wave-lengths from the speculum surface when a first-order colour appeared at the centre. The pressure was now removed causing a still further separation, nevertheless a current easily measurable with the milliammeter was obtained with one dry cell. If the lens was tilted by shifting the weight, the gold surface was brought into closer proximity to the speculum surface on one side of the ring system, and the ammeter indicated an increase of conductivity. This experiment is very easily repeated, and appears to be free from objection, but unfortunately it is not well adapted to quantitative work on account of the variable distance due to the curvature of one of the electrodes.

At this stage of the work I left Baltimore, taking it up again at my East Hampton laboratory. Using a D'Arsonval galvanometer I have obtained currents with much greater separation of the plates. By shaking up lycopodium in a jar and allowing the spores suspended in the air to settle on a speculum plate, I have succeeded in obtaining a very satisfactory series of readings by squeezing the plates together with a micrometer screw, the spores being quite compressible. In spite of the fact that they are very resinous and probably good insulators we have the possibility of absorbed moisture.

Similar results were obtained when the speculum flats were separated with small flakes of very thin mica. The flakes were freshly split, their thickness determined with the spectroscope, and they were torn to pieces with ivory forceps to avoid the possibility of metallic contamination, which might result if scissors were used. In all cases I find evidences that metallic conduction commences with one volt of applied potential when the plates are between 20 and 30 wave-lengths apart, but this distance can be accurately measured only when semitransparent metallic films are used, so that my results have not been very consistent.

I have worked with the speculum plates mounted in the interferometer, and though I have obtained conduction before the plates appeared to be in contact, it appears to me that the separation can be much greater when mica flakes are present than when the gap is quite free from all material. With clean mica flakes pressed between the plates I have obtained conduction when light is still freely transmitted through the crevasse. With the plates mounted in the interferometer, however, the crevasse transmits little or no light when conduction commences. The light is of a deep blue colour, which is an interesting observation, as showing that a narrow crevasse refuses transmission to the long waves first. The colour effect is doubtless the result of the circumstance that the light which gets through has suffered multiple reflexions, though the same thing would doubtless be observed, though to a less degree, with a metal having no selective properties.

Upon the whole I feel disposed to believe that the experiments indicate that the effect is a real one, due possibly to the presence of an atmosphere of electrons in the immediate proximity of metallic surfaces. I realize, however, that it will be necessary to carry out to a successful conclusion the experiment with the semitransparent films before any definite conclusion can be reached; for there seems to be evidence that the presence of a solid dielectric such as mica or quartz dust increases the effect.

XXVIII. *Notices respecting New Books.*

The Structure of the Atmosphere in Clear Weather. A Study of Sounding with Pilot Balloons. By C. J. P. Cave, *M.A.* Cambridge, at the University Press, 1912. Pp. xii + 144.

THE book deals with observations made between January 1907 and March 1910 on 200 balloons sent up by the author, mostly from Ditcham, Hampshire. A few were of the "ballon sonde" type carrying instruments, but the large majority were true "pilot" balloons, *i. e.* carried no instruments, and served solely to give information as to the direction and velocity of the wind at different levels. The balloons were observed sometimes with two theodolites, at the ends of a measured base, sometimes with one theodolite only. In the latter event the rate of rise of the balloon must be supposed known. Usually it seems to have been assumed to be uniform. The balloon was recovered in some 30 per cent. of the cases, after travelling in several instances over 150 kilometres. Pp. 109–141 consist entirely of diagrams, showing the results obtained for the direction and velocity of the wind in selected cases, with the corresponding distribution of wind and barometric pressure at ground level over Western Europe. In addition there are 47 illustrations in the text. Theoretical questions are somewhat lightly dealt with, but there is a good deal in the book likely to interest meteorologists and aeronauts.

Monographs on Topics of Modern Mathematics, relevant to the Elementary Field. Edited by J. W. A. YOUNG. Longmans, Green & Co.: New York & London, 1911.

PROFESSOR YOUNG's aim in the preparation of this series of monographs is to bring within reach of secondary teachers and college students "a scientific treatment of some of the regions of advanced mathematics which have points of contact with the elementary field." There are nine monographs in all, each contributed by a different writer. Oswald Veblin writes on the foundations of Geometry, Holgate on Modern Pure Geometry, and F. S. Woods on non-Euclidian Geometry. Then we have the fundamental propositions of Algebra treated by Huntington, and the algebraic equation by G. A. Miller. G. A. Bliss follows with a discussion of the Function Concept and the fundamental notions of the Calculus; and Young himself contributes a memoir on the Theory of Numbers. L. E. Dickson discusses Constructions with Ruler and Compasses; Regular Polygons; and the book closes with the History and Transcendence of π by David Eugene Smith. The authors are all men of repute in the mathematical world; and their conjoint work has undoubtedly fulfilled the object aimed at. It does not require a large acquirement of mathematical knowledge for an intelligent reader to benefit by the perusal of its pages. Yet he will not find it altogether easy reading. Many of the processes and proofs have not yet found their way into the recognized textbooks the aims of which are practical rather than logical. It is important, however, that teachers of mathematics should have some knowledge of the logical foundations of the science they teach; and a better introduction could not be put into their hands than this series of tracts, which, though written by different authors, form a remarkably united sequence.

XXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 207.]

December 6th, 1911.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'Geology of a Part of Costa Rica.' By James Romanes, B.A., F.G.S.

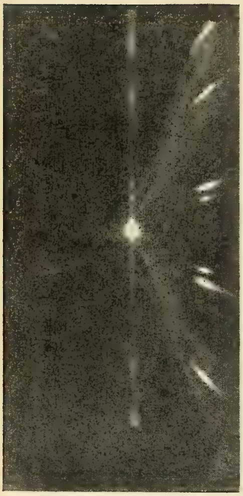
The paper deals chiefly with that part of Costa Rica which lies to the west of San José as far as the Pacific coast. San José itself is situated in a wide valley sloping gently westwards, and drained by the Rio Grande and its tributaries (defined in the paper as the San José Valley). The northern boundary of this valley is the chain of recent volcanoes which rise gradually from its floor, while on the south the ground rises abruptly to form the Cerro Candelaria.

In this latter range of mountains are exposures of limestone, marl, etc., together with various igneous rocks. The limestone is that which is referred to the Cretaceous by R. T. Hill; but an examination of several exposures has failed to produce any Cretaceous fossils, while the occurrence in places of vast numbers of *Balani* points to a Tertiary age for the beds. As this limestone stretches right across the Atlantic-Pacific watershed between Cartago and San José, it yields clear evidence of an interoceanic connexion in this area in Tertiary times.

Of the igneous rocks, the most interesting feature is the presence of many boulders of monzonite, indicating a plutonic mass in these mountains. The surface of the San José Valley is composed of a thick series of andesitic lavas into which the rivers have cut deep gorges, exposing in some cases older river-deposits and buried spurs of the Cerro Candelaria. On the Pacific coast at Barranca and Manzanilla fossiliferous Tertiary beds are described. These are all marine ashes, and in the Manzanilla district appear to rest unconformably on an older limestone-formation. From the same area a limburgite is recorded.

The dominant features of the Pacific shore-line are due to drowning, instead of to uplift as is the case on the Atlantic coast; these features have, however, been considerably modified by subsequent alluvial deposits.

The 'boulder-clays' of Costa Rica are shown in many cases to be normal river-deposits, though locally landslides and spheroidal weathering have played an important part. These deposits in the valley of the Rio Reventazon point to several distinct phases of river-action.



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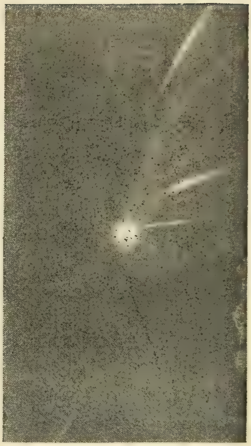


FIG. 3.

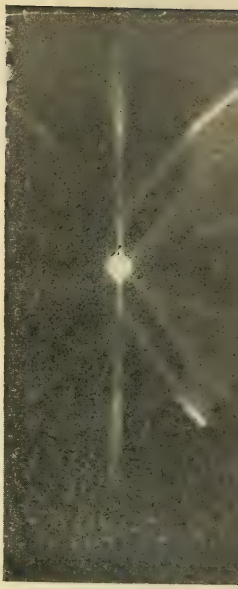
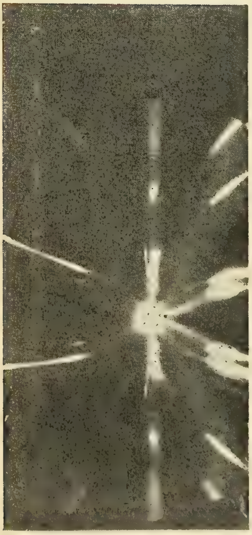


FIG. 4 *b*.



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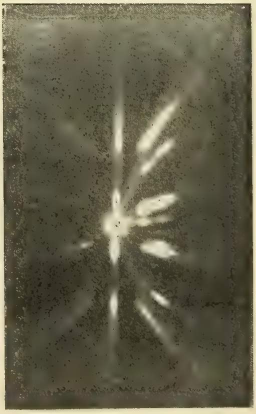

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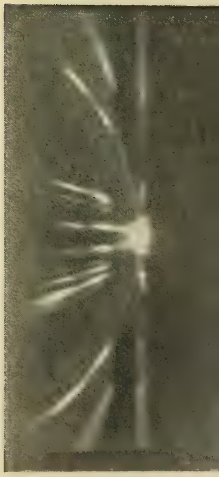

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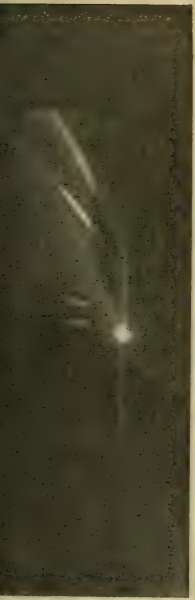

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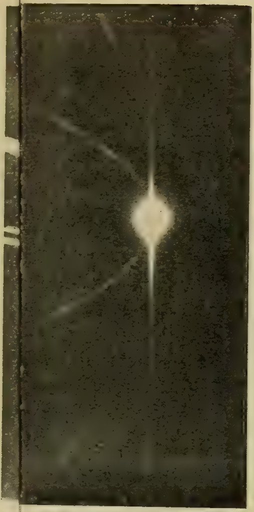

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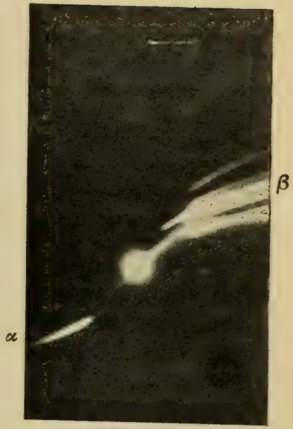

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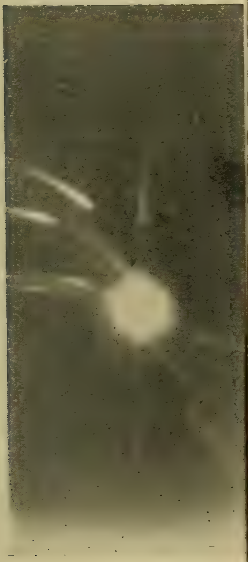

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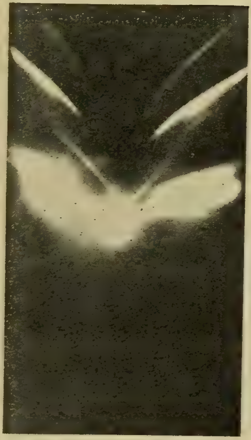
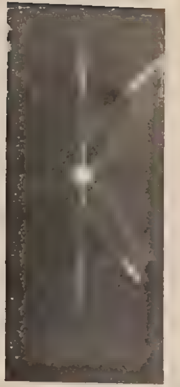


Fig. 21 *c*.

Fig. 28.

Fig. 2.

Fig. 3.



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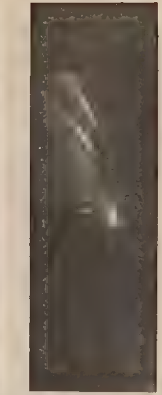

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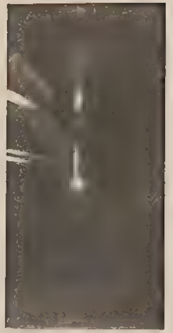

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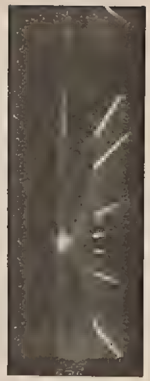

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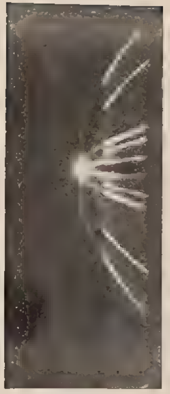

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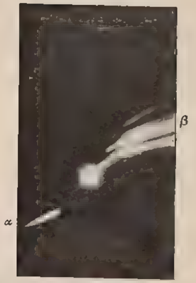

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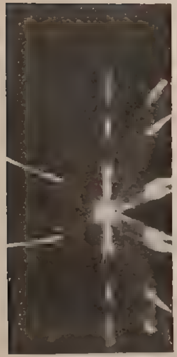

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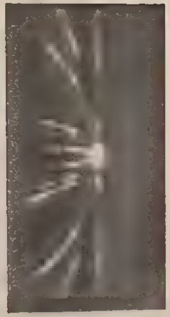
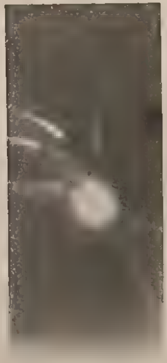


Fig. 16 *a*.



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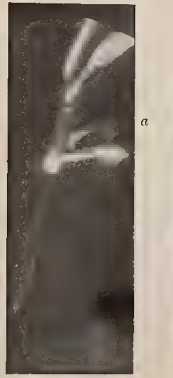
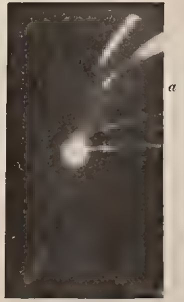


Fig. 21 *a*.



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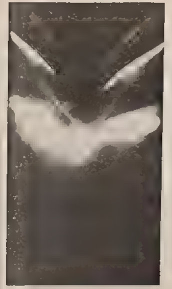

Fig. 21 *c*.

Fig. 28.

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[SIXTH SERIES.]

SEPTEMBER 1912.

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XXX. *Mathematical Analysis of some Experiments in Climatological Physiology, &c.* *By* G. H. KNIBBS, *C.M.G., F.S.S.*[*]

1. General.
2. Computation of "Dryness."
3. Theory of Evaporation from Circular Tank of Limited Dimensions.
4. Application to Human Body.
5. Increase of Loss due to Wind.
6. Evaporation Formula for Water in Tanks.
7. Nature of Formula for Wind Effect.
8. Thermodynamic Elements of the Formula.
9. Difficulties of Analysis.
10. Principle of deducing a Formula.
11. Desirable to use Saturation-Deficit as argument.
12. Deduction of Formula for Total Loss.
13. Losses of Water and Carbon Dioxide.
14. General indications for further investigation.

1. *General.*

PROFESSOR W. A. OSBORNE, in the 'Journal of Physiology' (vol. xli., 31st December 1910, pp. 345–354), has furnished for different temperatures and degrees of humidity the results of a number of carefully made observations on the rate of loss from the bodies of two persons, viz. W. A. O. and A. C., the actual conditions being those to which the human body is ordinarily subjected. A cursory inspection of these results shows marked divergencies under similar conditions, and discloses the fact that a merely empirical interpretation is of little practical value. Some general view of the evaporation from the human body must therefore be established so as to furnish a basis for a rational formula. With this in view we may consider primarily the phenomena of evaporation from the surface of a liquid into air containing more or less aqueous vapour. Unfortunately no adequate theory of this has yet been developed.

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[*] Communicated by the Author.

Rates of evaporation from a liquid into air depend upon pressure, upon temperature, upon the degree of saturation of the surrounding atmosphere, and upon the mechanical motion of the vapour over the liquid. No doubt evaporation from a human body differs in many essential particulars from this phenomenon; nevertheless, one may reach some view as to the proper type of formula for correlating evaporation from the body with temperature and dryness by reference to evaporation under like conditions from water.

In the first place, we may remark that in the phenomena with which we are concerned, the temperatures are far *below* the point of ebullition, and at such moderate temperatures (say below 50° C.) the total pressure or content of aqueous vapour in the air amounts absolutely only to a small quantity, ranging from

		inches	mm.		grains		grammes	
0° C.:	Pressure	0·180	4·57	Weight	2·113	per cub. ft.	4·835	per cub. metre.
40° C.:	„	2·160	54·87	„	22·125	„	50·625	„ „
50° C.:	„	3·621	91·98	„	?	„	?	„ „

that is, say 50 parts in 1 million for 40° C.

When superincumbent air is saturated, however, the molecular interchange of the vapour of the liquid from the liquid to the air is equal to that from the air to the liquid, and the relative quantity of the vapour is measured by the weight per unit volume, which is approximately proportional to the pressure of the vapour in the air. Hence the velocity of diffusion increases with the dryness of the air. We note also that at the same conditions of temperature and pressure, the density of water-vapour is only 0·6221 that of air, and this affords some mechanical assistance to the velocity of diffusion.

It is clear from these considerations that we may regard the phenomenon of loss as correlated to the three factors, viz., air temperature, dryness, air movement. For the measure of the air temperature and the dryness we need the reading of dry and wet bulb thermometers; under, however, definite conditions as to movement of the wet bulb, or as to a current of air flowing about it. These conditions were realized in the experiments so far as the measurement of dryness is concerned.

In considering the phenomena of losses of weight through evaporation from the skin, and losses of water and carbon through the respiratory apparatus, the following conception will be of service :—

The human body is, within certain limits, a fairly well and automatically regulated thermostat. In general it is immersed in air of a lower, very rarely of a higher temperature. On the principle of transfer of heat without change of state, therefore, it would tend, if other factors did not operate, to fall slightly below a certain critical value, say $\mathfrak{T}_c$, in air of lower temperature than the body, and to rise above this temperature in air of higher temperature. The value of $\mathfrak{T}_c$ is peculiar to the individual and can be taken as having a definite value only as the mean of a large number of individuals. $\mathfrak{T}_c$ is thus somewhere about 37° C., or 98° to 99° F.

In the mechanical and chemico-physical arrangements of the human thermostat, however, actions supervene after about say 30° C. (86° F.) is reached, which disturb those conditions of thermogenesis and thermolysis which are necessary for the thermostasis of the organism; that is to say, the whole condition tends thermostatically to become more or less labile.

Within the limits of thermostatic stability the mechanism, for the purposes of physical representation, may be regarded thus :—

Heat is generated within the organism, mainly by combination of carbon with oxygen brought by the blood. This carbon is eliminated chiefly by the means of the respiratory apparatus. Water is also given out, in the form of vapour, by the respiratory system. These two may be called the chief elements of the respiratory losses. Besides these are minor anthropotexic products which, from the merely quantitative point of view, may be regarded as negligible.

Besides these losses, there is loss, chiefly of water, through the skin. For the purpose of representing this loss, we may regard the skin as a porous wall backed by capillary vessels by means of which the moisture is supplied. These capillaries, however, are profoundly affected both by physical conditions without (*e.g.* by cold, produced by wind-cooling or otherwise), and by physiological conditions within.

The elimination of heat-energy from the body is effected, where the surrounding air is cooler, by radiation, by convection losses (since the film of air next the body is heated and distributed by convection), and by the conversion of water into vapour. The abstraction in this way of the necessary quantity of heat from the body prevents its accumulation therein and a consequent undue rise of temperature.

The phenomena of diaphoresis show that the quantity of water eliminated by the skin may vary between somewhat wide limits. If the body be in a truly thermostatic condition the quantity eliminated by evaporation from the skin-surface will not necessarily be constant in rate for like external conditions. If the rate of thermogenesis, however, does not vary it will be constant, but where this rate changes, the evaporation rate will so respond within the stable limits as to tend to maintain the thermostatic equilibrium, always, of course, approaching this equilibrium state asymptotically.

As the temperature of the air approaches that of the body, the radiational and convectional losses become small, then zero, and finally negative. Heat tends to pass from the air to the body. In ordinary cases it actually does not so pass, for the air is not ordinarily saturated with vapour, and when this is the case the external conditions are such that heat may still be abstracted from the body by the conversion of water into aqueous vapour.

The increase of temperature operates to make the molecular action concerned in converting liquid H_2O into gaseous H_2O, more active, but in all ordinary conditions the absolute capacity of the air for water vapour is greatly augmented as the temperature rises. Thus in millimetres pressure the increase is as follows, viz.:—

Degrees centigrade...............	0–1	10–11	20–21	30–31	40–41	50–51
Difference Pressure—Aqueous vapour mm. for 1° C	0·34	0·63	1·11	1·86	3·00	4·68

The difficulties of maintaining thermostatic equilibrium thus tend to increase as the condition changes from the transfer of heat by means of evaporation, together with radiation and convection, to the condition when the whole elimination of heat is by evaporation. For in the latter case the rate at which heat is abstracted from the body has to compensate for the heat tending to flow into it from the hotter air surrounding it. This explains the enormous influence of dryness (or defect from complete saturation) as the temperature of the body is approached or exceeded by that of the air.

The rapidity with which the state of the human body changes indicates that the analogue of a porous vessel is inadequate, and in even the most carefully conducted experiments, considerable discrepancy from any simple progression of results, corresponding to progression in the conditions, is to be expected. For this reason secure deductions must perforce be based upon means of a large number of results.

With regard to any attempt at a mathematical solution from first principles, it may be pointed out that the spatial form of the surface of the body is too complex to admit of definite geometrical representation. Thus any attempt to deduce theoretically the complete form of the function representing the evaporation, when the discharge of the aqueous vapour into the air may be assumed to be by diffusion, and to quantitatively estimate it, will be hopeless. The only practical hope is to base a view of evaporation from a human body on the observed phenomena of evaporation from a water surface, or better still, from the observation of evaporation-losses from a porous surface kept continually moist by a copious supply of water beneath it. In fact the observation of such loss carried on simultaneously with experiments on the human body would doubtless be of high value, since it would reveal any departure arising from the physiological reactions supervening with increasing heat.

In considering evaporation-losses either from the body or a porous surface, it is necessary to distinguish the conditions under which the aqueous vapour formed finds its way into the atmosphere regarded as of unlimited receiving capacity.

If wholly by diffusion, the process would be relatively very slow and the rate would be profoundly affected by the equipressural surfaces and the orthogonal trajectories thereto indicating the lines of maximum flow. But aqueous vapour has a density of only 0·6221, air being taken as unity. Hence it will tend to rise at a velocity depending on this difference of gravitational pressure. Further, the body itself sets up convectional currents, and movements in air: hence the diffusion tends to be accelerated, and the characteristics of the distribution of the aqueous vapour into the air tend to be less dependent on the form of the surface. That is to say, other things being equal, each unit of surface becomes more nearly identical in contributing to the total evaporation.

It is important further to distinguish the conditions obtaining in regard to the losses from the respiratory apparatus, and through the skin. By the mechanism of the respiratory apparatus, air being taken into the lungs is warmed or cooled, as the case may be, approximately to the temperature of the body, say to about 37° C. Hence its capacity for absorbing water would appear to depend sensibly on the difference between the total capacity of air at that temperature and on the original defect from complete saturation. Now the capacity for saturation of air at say 37° C. is 46·65 mm., which implies generally a considerable margin for taking up moisture from the body.

The loss of carbon doubtless depends upon the rate of metabolism, and hence may be expected to show considerable changes from its mean value towards the limiting conditions, viz., for very high and very low temperatures.

The resolution of the matter must therefore, in its essence, be mainly empirical. The function expressing rate of evaporation ought probably to deal with evaporation losses from the skin and from the lungs separately, as well as losses of carbon from the lungs. The data must be temperature, capacity of the air for further saturation, the condition of air movement, and characteristics of the body (viz., weight, form, and other special characters). With these a quantitative solution is possible, but the type of formula necessary must be deduced from the results and their rational interpretation, and not wholly *à priori*.

Although within certain limits the body may be regarded as a thermostat, its surface is by no means thermostatic, and its variations of temperature depend not only upon the temperature of the surrounding air but also upon the air movements on the surface of the body. Apart from the consequences arising from the difference in temperature of the liquid at the surface of the body, no doubt the reactions on the arterioles and capillaries profoundly affect the conveyance of liquid to the surface. In fact, we have an evaporating surface with considerable variations of temperature and degrees of porosity, reacting quickly to external and internal conditions.

Thus in any complete solution on first principles we should have to take into account the mean temperature of the surface, and its variations with air temperature and air movement.

It will on the whole be probably more convenient to regard these conditions as among the physiological elements of variation, since in any conceptual case (taken to represent the phenomena) the body must be supposed in the same state for identical external conditions, any physiological factor being treated independently. The temperature of the evaporating surface is probably in all cases sensibly less than 37° C. by an amount which itself depends on the temperature, saturation capacity, and movement of the air. Hence in an empirical solution we may include these elements in the factors representing external conditions. They will influence the form of the functions representing the effect of these elements.

2. *Computation of Dryness.*

To calculate the dryness we may proceed as follows:—If s denote the specific heat of air at constant pressure, $= 0{\cdot}2374$ (Regnault); l the latent heat of water at temperature t, $=607-0{\cdot}708\,t$ (Clausius); r the relative density of aqueous vapour as compared with air $=0{\cdot}6221$ about; P the barometric pressure, the units being metric, then, according to the Ivory-August-Apjohn formula, the pressure f' of aqueous vapour in the air is

$$f' = f - \frac{s\,.\,P}{r\,.\,l}(T-t), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

f being the saturation-pressure at temperature t, and f', f, and P being measured in the same units. Let F denote the saturation-pressure at temperature T, viz. that of the dry-bulb thermometer, as f denotes the saturation-pressure at the temperature t of the wet-bulb thermometer; then the relative humidity is measured by the ratio

$$\mu = \frac{f'}{F} = \frac{f - \frac{sP}{rl}(T-t)}{F} = \frac{f-q}{F}, \text{ say}, \quad . \quad . \quad (2)$$

where q is a tabular value of $sP(T-t)/rl$. It is found that with moderate velocities of motion of the wet-bulb thermometer the value of q is as follows:

$$q = 0{\cdot}000660\,P\,(T-t)\left(1+\frac{T-t}{873}\right), \quad . \quad . \quad . \quad (3)$$

which has been tabulated *.

Since the relative dryness η is zero for saturated air, and unity for perfectly dry air, we may adopt the definition, relative humidity plus dryness equals unity. Hence

$$\eta = 1 - \mu = 1 - \frac{f-q}{F}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus for practical working F and f may be taken from Table 43, p. 142, and q from Table 44, p. 143, of the third revised edition (1907) of the Smithsonian Meteorological Tables.

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* An important article on "The Pressure of Saturated Vapour from Water and Ice as measured by different authorities" is given by Prof. C. F. Marvin in 'Monthly Weather Review,' Jan. 1909, pp. 3–9. See also the Bibliography, *ibid.* p. 9.

An example will illustrate: the degrees are centigrade; assumed pressure 760 mm.,

$$T = 27{\cdot}2\,; \quad t = 16{\cdot}7\,; \quad T - t = 10{\cdot}5.$$

From Table 43 we have for $T = 27^{\circ}{\cdot}2$ C., 26·78 mm.; and for $t = 16^{\circ}{\cdot}7$ C., 14·12 mm. From Table 44, for $T - t = 10^{\circ}{\cdot}5$ C. and pressure 760 mm., we have by interpolation between 10 and 11, 5·34; hence for the relative dryness we have

$$\eta = 1 - \mu = 1 - \frac{f-q}{F} = 1 - \left(\frac{14{\cdot}12 - 5{\cdot}34}{26{\cdot}78}\right) = {\cdot}672. \quad (5)$$

In this way the quantities η shown in the tables of data were calculated for the whole of the observations.

It is no doubt desirable to base the formula for evaporation from a body not on the relative but on the absolute capacity, ζ, for further absorption of aqueous vapour in the air. This would be

$$\zeta = F\eta = F - f + q, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and may be called the absolute dryness or saturation deficit. The rate of such absorption would then be regarded as depending on the temperature, as well as on the exhaustion of this capacity for absorption.

Three methods of taking account of the effect of dryness in promoting diffusion suggest themselves, viz., making the rate of evaporation a function of:—

(*a*) The temperature and relative dryness; or
(*b*) The temperature and absolute dryness (or amount necessary to saturate the air at the temperature in question); or
(*c*) Temperature and the difference of reading between the two bulbs.

We shall now consider the question of evaporation from a liquid in a circular tank of small dimensions, and its applications to the matter in hand. The data, and calculations based thereon, furnishing measurements of total loss from the human body, are the following:—

TABLE I.

No. (1)	Temp. air dry bulb T° C. (2)	Temp. air wet bulb t° C. (3)	Diff. $(T-t)$° C. (4)	Relative dryness. η. (5)	Absolute dryness. ζ. (6)	Loss in grms. (7)	Loss calc. (19) (8)	Loss calc. (19a). (9)	Weight in kilos. (10)	Diff. obsd. −calc. (19a). (11)
1	15·0	11·6	3·4	·333	4·23	60	31	54	68	+ 6
2	17·0	13·5	3·5	·324	4·67	47	...	...	46	...
3	17·3	13·6	3·7	·338	4·96	50	41	57	68	− 7
4	17·5	13·9	3·6	·329	4·87	74	41	57	,,	+17
5	18·9	14·6	4·3	·371	6·04	62	51	61	,,	+ 1
*6	19·0	12·6	6·4	·533	8·70	98	...	...	,,	...
*7	19·3	14·6	4·7	·401	6·65	67·5	...	...	,,	...
8	20·2	15·0	5·2	·429	7·53	62	62	67	68	− 5
9	20·2	14·4	5·8	·674	8·32	79	65	70	,,	+ 9
10	21·0	14·5	6·5	·515	9·48	88	73	74	,,	+14
11	21·1	17·6	3·5	·291	5·40	44	54	61	,,	−17
*12	21·1	13·0	8·1	·624	11·54	68	...	...	,,	...
13	21·7	15·0	6·7	·519	9·99	89	78	77	,,	+12
*14	21·7	12·5	9·2	·683	13·15	98	...	...	,,	...
15	22·5	18·3	4·2	·333	6·74	80	66	67	68	+13
16	22·8	16·3	6·5	·492	10·12	61	...	...	46	...
17	23·3	13·8	9·5	·674	14·33	72	103	95	68	−23
18	23·9	15·0	8·9	·630	13·86	76	102	95	,,	−19
19	23·9	13·2	10·7	·735	16·18	55	...	...	46	...
20	25·0	14·6	10·4	·700	16·45	87	118	107	68	−20
21	26·1	17·7	8·4	·571	14·31	95	111	101	,,	− 6
22	27·0	18·0	9·0	·595	15·70	107	120	109	,,	− 2
23	27·2	20·5	6·7	·459	12·26	106	105	95	,,	+11
24	27·2	20·0	7·2	·507	13·06	112	108	98	,,	+14
25	27·2	16·7	10·5	·672	18·00	107	132	119	,,	−12
26	28·9	20·5	8·4	·537	15·74	108	126	114	68	− 6
27	29·2	17·0	12·2	·728	21·90	152	156	142	,,	+10
28	30·5	17·8	12·7	·733	23·76	123	...	...	46	...
29	31·7	16·5	15·2	·822	28·53	157	195	183	68	−26
*30	32·8	18·8	14·0	·757	27·97	252	...	...	,,	...
*31	33·6	18·1	15·5	·805	31·14	235	...	...	68	...
32	34·0	20·0	14·0	·742	29·30	230	206	197	,,	+33
*33	35·0	19·1	15·9	·802	33·49	275	...	...	,,	...
34	35·7	19·7	16·0	·796	34·57	181	236	233	,,	−52
*35	35·8	20·0	15·8	·788	34·39	362	...	...	46	...
36	36·1	21·1	15·0	·822	33·48	284	232	229	68	+55
37	37·0	20·0	17·0	·814	37·99	270	256	260	,,	+10
38	37·2	20·0	17·2	·819	38·60	254	260	264	,,	−10
39	38·3	21·1	17·2	·805	40·29	212	...	...	46	...
*40	39·4	21·1	18·3	·827	43·93	323	...	...	68	...

* These results are influenced by wind, and have been omitted in attempts at analysis.

3. *Theory of Evaporation from Circular Tank of Limited Dimensions.*

Under similar circumstances regarding the elements which affect diffusion, the rate at which the vapour is given off from a liquid depends on the absolute temperature. According to Stefan's investigation (*Abhandl. Akad. Wien*, 1881; *Journ. de Phys.* 1882, p. 202) the rate of formation of vapour in a circular vessel of small dimensions is proportional, however, to the lineal and not to the areal dimensions of the surface. The lines of flow of the vapour are a system of hyperbolas, the foci of which are on the bounding edge of the liquid, and the orthogonal trajectories of which (ellipsoids) constitute the surfaces of equal pressure. Since these are closest together at the margin of the liquid and least close directly over its centre, the flow is greatest at the edge, and least immediately over the middle.

These results represent what would take place where there was no physical motion of the air over the liquid. In all actual cases, however, apart from the vortical disturbances of the air due to the motion generated by the sources of heat, there are other air disturbances; and even when these are moderate, there can be no doubt that the conditions are completely changed, and the theory in its integrity becomes inapplicable. Thus A. Winkelmann's (Wied. *Ann.* xxxiii. & xxxv., 1888) attempt at experimental verification was not successful, though he regarded the failure as not attributable to defect in Stefan's theory. This theory of Stefan's leads to the formula

$$E = 4kr \log_e \frac{P-p''}{P-p'}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where E is the quantity evaporated per unit of time, k is a constant, r is the radius of the surface, P is the atmospheric pressure, p' that of the vapour at the surface, and p'' that at a considerable distance, say the ordinary pressure in the air of the vapour. That is, under the conditions supposed the quantity varies as the diameter, not (as one might suppose) as the area. It is obvious, however, that with considerable air-disturbance the rate of evaporation will more nearly approach the ratio of area, since the diffusion conditions become more nearly similar for each unit of surface-area.

4. *Application to Human Body.*

The equipotential surfaces about a human body in still air would be very complex in form; and if they could be treated by mathematical theory, that theory would furnish results which air-disturbance would vitiate even more than in the case considered by Stefan. They thus suggest that the area and not the mass of a body should be the quantity used in comparing results from different human beings. See, however, the result hereunder.

Two persons similarly built, differing only in linear dimensions, would weigh as the cubes of any common measurement (*e. g.* their height), while the surface of their bodies would vary as the square of the common measurement. If, therefore, we regard the loss as occurring mainly by evaporation from the skin-surface, it should vary, other things being equal, as a function of the weight (lying between say the $\frac{2}{3}$rd power to the $\frac{1}{3}$rd power, most closely approximating to the former), because of air-disturbances which make the evaporation from each part comparable to that of any other part. Hence we should regard the factor to determine the absolute loss not as W, the weight of the person, but rather as a quantity approaching $W^{\frac{2}{3}}$.

This may be roughly tested by the experiments with W. A. O. and A. C. (which, however, do not give the index two-thirds but give one-third) as follows :—

First eliminating all observations which appear to give results divergent from the general trend, we have the following for the body-weights 46 and 68 kilograms, viz. :—

TABLE II.

Weight of body 46 kilos.			Weight of body 68 kilos.		
Temp.	Dryness.	Loss in grammes.	Temp.	Dryness.	Loss in grammes.
17·0	·324	47	17·3	·338	50
22·8	·492	61	23·3	·674	72
23·9	·735	55	23·9	·630	76
30·5	·733	123	29·2	·728	152
35·7	·796	181	34·0	·742	230
38·3	·805	212	37·2	·819	254
Mean 28·0	·647	113·2	27·5	·655	129·0
(Less $C+H_2O=22{\cdot}0$) =		91·2	(Less $C+H_2O=22{\cdot}0$) =		107·0

91·2 : 107·0=1 : 1·173,
113·2 : 129·0=1 : 1·138,

46 : 68 =1 : 1·478,
$(46:68)^{\frac{1}{3}}=1:1{\cdot}139$
$(46:68)^{\frac{2}{3}}=1:1{\cdot}297$.

It will be seen from these results that, so far as they may be relied upon, the loss is not as the weights, nor even as the surface-areas of the two bodies submitted to experiment, but as the linear proportions (1·138 and 1·139), thus apparently agreeing with Stefan's theory. So close an agreement, however, must be regarded as quite fortuitous, and it is questionable whether it should be relied on. Further, if we subtract the loss of carbon (6·2 grms.) and water (15·8 grms.) from the lungs (22·0 grms. in all), so as to get the net loss through the skin, it does not sensibly alter the result.

5. *Increase of Loss due to Wind.*

Professor Osborne's experiments disclose the relatively large effect of wind readily enough. Taking out results under sensibly similar conditions as to temperature and dryness, we see that the effect is well marked, so much so that any effective analysis of quantitative results without measures of wind velocity is out of the question.

TABLE III.

Temp. C.	Relative dryness.	Loss with no wind. grammes.	Temp. C.	Relative dryness.	Loss with wind. grammes.
18·9	·371	62	17·5	·329	74
20·2	·674	79	21·7	·683	98
23·3	·674	72	23·9	·630	76
31·7	·822	157	32·8	·757	252
34·0	·742	230	33·6	·805	235
35·0	·802	275	35·8	·788	362*
37·2	·819	254	39·4	·827	323†
Mean 28·6	·701	161·3	29·2	·688	202·9

* Strong breeze. † Less breeze.

Bearing in mind that evaporation by diffusion is slow, and varies (apparently) as a linear element of the exposed surface, we see that the data for any satisfactory solution must include wind velocity, or rather velocity of air movement about the body subjected to experiment.

These quantities found above (viz. 161·3 and 202·9) represent the means in grammes per hour of the loss in a man weighing 68 kilogrammes respectively in sensibly still air and in a breeze, and they are in the ratio of 100 to 126. The temperatures, viz. 28°·6 and 29°·2, and relative dryness 0·701 and 0·688 are sensibly equal and do not account for the great difference of loss.

6. *Evaporation Formula for Water in Tanks.*

The reality of this increase of evaporation through wind is implied in the empirical formulæ of Abbassia, Carpenter, Fitzgerald, and Stelling, all of whom give for E the rate of evaporation from an indefinitely large surface of water.

$$E = k(f''-f''')\{1+k'V\}, \quad . \quad . \quad . \quad . \quad (8)$$

in which f'' is the vapour saturation-pressure of the surface of the water, f''' is the saturation-pressure for the dew-point, and V denotes wind velocity. There is, however, no sort of agreement among the constants given.

As far back as 1867 Tacchini gave a formula of the type

$$E = aT - b\mu + cV, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

V denoting velocity of wind; and also further gave a formula,

$$E = aT - b'\mu + c'V - d\nu + e\sin h, \quad . \quad . \quad . \quad (10)$$

where ν is the cloudiness in hundredths of the sky obscured, h is the meridian altitude of the sun *.

A. Weilemann in 1877 gave a formula which may be written

$$E = \frac{AM}{a+k}(1+kV), \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which A and k are constants determined from observations; V is wind velocity; a is the change in the vapour-tension of saturated air at the temperature of the experiment for 1° C.; M is the saturation-deficit (in grammes per cubic metre) †.

In 1885 F. Houdaillie submitted a formula, viz.:—

$$E_v = \frac{E_0}{1+0{\cdot}5V} + \frac{25{\cdot}1(F-f)}{1+0{\cdot}24(F-f)}(V+5\sqrt{V}), \quad . \quad (12)$$

in which E_v is the evaporation for velocity V; E_0 is the evaporation in still air; F and f are the differences of the vapour saturation-pressure for the water temperature and the vapour-pressure in the air ‡, in relation to the effect of wind velocity, &c.

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* *Bull. Met. Oss.* iii. pp. 1–10, 17–19 (1867).

† *Schweiz. met. Bebb.* xii. pp. 268–368.

‡ *Comptes Rendus,* ci. pp. 428–431 (1885).

Some of the deductions of Houdaille are very important; for example, that

(*a*) Increase in rate of evaporation with air movement is very rapid for low velocities, but becomes sensibly proportional to the wind velocity when it attains 4 metres per second ;

(*b*) The increase is independent of the difference between the vapour-tension at the water surface and that of the air ;

(*c*) Increase of evaporation due to solar radiation is sensibly proportional thereto ;

(*d*) The utilization of solar heat varies greatly according to temperature, humidity, and intensity of insolation ;

(*e*) Electric tension causes rapid increase of rate of evaporation *.

Schierbeck in 1896, in his article "Sur la vitesse de l'évaporation au point de vue spécial des relations physiologiques," † confirms Stefan's formula. He found that the coefficient of evaporation was directly proportional to the absolute temperature (see, however, reference to Marvin's work hereinafter), and he gave an expression for the volume of vapour passing through a cross-section of unit area in unit time at a temperature of 0° C. and pressure 760 mm.

More recently, after making a series of elaborate experiments at Paris, Prof. F. H. Bigelow submitted a somewhat elaborate formula in which there was a coefficient containing thermodynamic constants; a term denoting saturation vapour-pressure at the temperature of the water surface ; a term denoting the vapour-pressure at the dew-point of the surrounding air ; and a term depending on wind velocity : and he says :—"We have shown that the following terms enter vitally into an evaporation formula, viz., surface-water temperature, dry-bulb and wet-bulb temperatures, and velocity, and besides these there are apparently some unknown terms concealed in the thermodynamic coefficient" ‡.

In an article on a proposed new formula for evaporation §, C. F. Marvin points out that "absolute evaporation," viz., the number of molecules passing out of the water, varies as T/B, where T is the absolute temperature and B is the barometric pressure. But the effective or *apparent* evaporation is the "absolute evaporation" diminished by the number of molecules returning to the water. The higher the temperature of the air, the greater its capacity to receive and disseminate the moisture, and this is greatly facilitated by wind. Bigelow remarks that the rate of evaporation $d\mathrm{E}/dt$ may be discussed under two forms, viz.,

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* *Annales école nat. agric. Montpellier*, vi. pp. 197–247 (1892).

† *Overs. k. Danske Forhandl.* i. p. 30 (1896).

‡ Monthly Weather Review, 1908, p. 445.

§ Monthly Weather Review, February 1909, pp. 57–61.

$$\text{(i.)} \quad d\mathrm{E}/dt \quad \text{varies as} \quad (\mathrm{T}_s \, . \, \mathrm{T}_a/\mathrm{T}_d)\frac{\mathrm{V}}{\mathrm{B}},$$

$$\text{and} \quad \text{(ii.)} \quad d\mathrm{E}/dt \quad \text{varies as} \quad (\mathrm{T}_s + \mathrm{T}_a - \mathrm{T}_d)\frac{\mathrm{V}}{\mathrm{B}},$$

in which T_s is the temperature of the water-surface, T_a that of the air, T_d that of the dew-point, measuring therefore the actual quantity of aqueous vapour; V is a measure of wind velocity and B of the barometric pressure. After showing how the Bigelow and Dalton equations are obtained from (i.) by neglecting certain elements among the conditions, Marvin submits the formula

$$\mathrm{E} = \mathrm{C} \, . \frac{e_s}{e_d} \, . \frac{\delta e}{\delta s}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

in which $\delta e/\delta s$ is merely the *tabular difference* in the ordinary table of saturated vapour-pressures for successive temperatures, representing thus the rate of change with temperature corresponding to the temperature of the water-surface; e_s is the saturation vapour-pressure corresponding to T_s, and e_d is the saturation vapour-pressure corresponding to T_d. C/e_d therefore varies with wind-velocity and dryness. Marvin remarks that "evaporation by pure diffusion takes place only in perfectly quiescent air, and we know the process is a very slow one." Hence he concludes that in all ordinary cases the wind velocity must be taken into account, in all open air conditions, and indeed generally *.

7. *Nature of Formula for Wind Effect.*

In order to deduce evaporation results when the air is in movement, it will probably be found necessary to take it into account in two different ways. Thus, for example, wind, or air-motion, as influencing evaporation, may be supposed to have a dual action, viz. :—

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* An extensive bibliography of treatises on Evaporation by Mrs. Grace J. Livingston will be found in the Monthly Weather Review, 1908, pp. 184–186, 301–306, 375–381; and 1909, pp. 68–72, 103–109, 157–160, 193–199, 248–252.

(*a*) By disturbing the film of air saturated with aqueous vapour on the surface of the body it may ultimately render each unit of area equally potentially efficient in contributing to the total evaporation ;

(*b*) It may directly influence the quantity of evaporation.

Hence for (*a*) the formula must contain an expression

$$W^{\frac{1}{n}}, \quad \text{in which} \quad 2<n<3,$$

and n must be a function of wind velocity V say. In order that in this expression n shall be between the limits 2 and 3, we must have some such function as

$$n=2+e^{-mV^c}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

e being the base of the Napierian logarithms. The value of this is 3 when $V=0$, that is, when the saturated aqueous vapour-film next to the body has to distribute itself by diffusion. It also approaches 2 when V^c is large. The rapidity and characteristics of the rate of approach are determined by the magnitude of the constants m and c.

For (*b*) we may write $1+\psi(V)$, and must determine the form of the function by experiment. Probably

$$1+\psi(V)=1+kV-lV^2 \quad . \quad . \quad . \quad . \quad (15)$$

will be found satisfactory enough. This expression could be made to express the conditions required, as far as they are known, though its form cannot, in the nature of the case, be quite general. A formula to make the increase for the effect of wind velocity most rapid initially, and finally proportional to the velocity, would require to be of some such form as

$$1+\psi(V)=1+k\{V+a(1-e^{-bV})\} \quad . \quad . \quad (16)$$

(since the former expression can give only empirically the desired results for a limited range).

The constants k, a, b could be determined from the observations, and e is the base of the Napierian logarithms. The constant a would be small as compared with large values of V *.

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* For actual evaporation of water Professor C. F. Marvin believes that the effect of wind is ultimately to give an increasing value for dE/dV, that is, the graph of the curve with velocities of wind as abscissæ and evaporation as ordinates is concave upwards (see Monthly Weather Review, February 1909, p. 59). This would require the formula to be $1+kV-lV^2+mV^3$, but such formula would probably apply to water-surface only where wave disturbance was a feature.

8. *Thermodynamic Elements of the Formula.*

The thermodynamic elements of the evaporation formula depend upon the temperature and the dryness, relative η or absolute ζ. The proper formula for the case of evaporation etc. from the human body can be discovered only by experiment, since the skin action (and the lesser losses of CO_2 and H_2O from the lungs) is by no means identical with evaporation from a water-surface, owing to reactions of the peripheral nervous system. It would no doubt be theoretically preferable and probably practically advantageous to use the absolute temperature $\mathfrak{T}$ say. Hence, using ϕ_1 and ϕ_2 for the form of the functions for temperature and dryness, yet to be determined, we have for E the evaporation or loss per unit of time

$$\mathrm{E} = \phi_1(\mathfrak{T}) \cdot \phi_2(\eta)\{1+k[\mathrm{V}+a(1-e^{-b\mathrm{V}})]\}\mathrm{W}^{\frac{1}{n}} \qquad (17)$$

[where n has the value indicated in 17 a],

or else

$$\mathrm{E}=\phi_1(\mathfrak{T}) \cdot \phi_2(\zeta)\{1+k\mathrm{V}-l\mathrm{V}^2+m\mathrm{V}^3\}\mathrm{W}^{\frac{1}{2+e^{-m\mathrm{V}^c}}}. \qquad (17\,a)$$

See also (14), (15), (16). We can of course accept $\mathfrak{T}$ as $\mathrm{T}+273°$. Instead of ζ or η we might also use $\mathrm{T}-t$. It remains to deduce the form of the functions ϕ_1 and ϕ_2, and probably it is better to use ζ than η for reasons hereinafter indicated.

9. *Difficulties of Analysis.*

The difficulty in arriving at secure deductions as to the relative influence of increase of dryness or increase of temperature arises from the large differences, due to unrecorded factors affecting the results, as given by the observations themselves. For example, we have :—

Table IV.

Observation No.	Air Temperature.	Relative Dryness.	Absolute Dryness in mm.	Loss in grammes.
15	22·5 C.	·333	6·74	80
17	23·3	·674	14·33	72
37	37·0	·814	37·99	270
38	37·2	·819	38·60	254

That is, there is a loss of 8 and of 16 grammes less, though the conditions (so far as recorded) would lead one to anticipate larger results.

The clothing was the same for the first pair of results, and practically the same for the second pair of results.

It is obvious we can make no secure deductions from single observations. The fact that there are no observations at high temperatures when the dryness was small, greatly limits the possibility of accurately analysing the data, and shows the need of further observations. Results can probably be best obtained by suitably grouping results, for example, to show the progressive increase of dryness as the temperature is raised. The results it will be found lend themselves fairly well to such a determination, but are less satisfactory in any attempt to ascertain for the same temperature the effect of increasing dryness.

10. *Principle of deducing a Formula.*

When observations disclose considerable intrinsic inconsistencies, grouping will often assist in disclosing their general trend. The principle of reduction may be thus stated:—

In reducing observations showing discrepancies, the magnitudes of which are relatively large, it is to be remembered that the probability of values found for relatively small terms is also very small. Thus it follows that their inclusion is often unmeaning, unless they are indicated by theoretical considerations (*e. g.* that they are necessary terms in any rationally deduced formula). It is thus evident that "group means" will often more clearly indicate the trend of the evidence than will individual results, a fact of which advantage has often to be taken in the analysis of statistical data. The legitimacy of any term derived from group means may be roughly deduced by considering whether it lies within or without the range of the probable errors of the data on which it depends. If it be without, its significance is very questionable.

11. *Desirable to use Saturation Deficit as argument.*

With regard to the choice of the element by means of which the dryness of the air is to be quantitatively expressed in a formula, it is, for example, obvious that we could employ $\mathrm{T}-t$ or η, together with $\mathfrak{T}$, or else we could employ ζ. We reject, however, $\mathrm{T}-t$ since the complexity of the resulting function would be objectionable. We also may reject η because its absolute significance varies with T or $\mathfrak{T}$, and we shall show by an appropriate tabulation that this rejection is justifiable.

12. *Deduction of the Formula for Total Loss.*

In applying the method of means it will be necessary first to reject observations that would appear to be decidedly anomalous owing to wind velocity, and to arrange the balance (either individually or in group means) with like conditions of "relative dryness." In this way we obtain the following results from the data from W. A. O.

TABLE V.

No. of Observations (Mean of).	Temp. C.	Relative Dryness.	Absolute Dryness.	Loss.	Loss per 1° C.	Mean Temp.	Mean Loss.
1, 3, 4, 5 15	17·2 22·5 Incr. 5·3	·343 ·333 Mn. ·340	5·02 6·74 Mn. 5·36	61 80 Incr. 19	3·6	18·3	
10, 13 21, 23, 24	21·3 26·8 Incr. 5·5	·517 ·512 Mn. ·514	9·74 13·21 Mn. 11·82	88 104 Incr. 16	2·9	24·6	
[1, 3, 4, 5, 10, 13] [15, 21, 23, 24] (*a*)	[18·6] [25·7] [Incr. 7·1]	[·401] [·467] [Mn. ·434]	[6·60] [11·59] [Mn. 8·59]	[70] [98] [Incr. 28]	[3·9]	[21·8]	[81]
9, 17 25 (*b*)	21·7 27·2 Incr. 5·5	·674 ·672 Mn. ·673	11·33 18·00 Mn. 13·55	75 107 Incr. 32	5·8	23·5	86
20, 27 32 (*c*)	27·1 34·0 Incr. 6·9	·714 ·742 Mn. ·723	19·17 29·30 Mn. 22·55	120 230 Incr. 110	15·9	29·4	157
29 36, 37, 38 (*d*)	31·7 36·8 Incr. 5·1	·822 ·818 Mn. ·819	28·53 36·69 Mn. 34·65	157 269 Incr. 112	22·0	35·6	241

Owing to the anomalous character of the first two pairs, it is preferable to combine them. This gives the results shown above in brackets.

In computing the loss per degree we see that on the whole it increases with the temperature and with the relative or the absolute dryness, the relation, however, being non-linear in either case.

On referring to the preceding table it will be seen that the saturation deficit or "absolute dryness" (see Obsns. 33, 34 and 38, 39) may be an increasing quantity, though the relative dryness is a decreasing one. Hence absolute dryness is consequently in all probability the preferable quantity to employ as argument *. To test this a second combination of observations appeared to be desirable in which the ranges of temperature were as large as possible for the same "absolute dryness."

TABLE VI.

No. of Observation.	Temp. C.	Relative Dryness.	Absolute Dryness.	Loss Weight.	Loss per 1° C.	Mean Temp.	Mean Loss.
3, 5, 8 11, 15	18·8 21·8 Incr. 3	·379 ·312 Mn. ·352	6·18 6·07 Mn. 6·13	58 62 Incr. 4	1·33	20·0	60
17, 18, 20, 21 22, 23, 24, 25	24·57 27·15 Incr. 2·58	·644 ·558 Mn. ·601	14·74 14·75 Mn. 14·74	83 108 Incr. 25	9·68	25·9	95·5
27, 29, 32, 38 26, 36, 37	33·02 34 Incr. ·98	·785 ·724 Mn. ·759	29·58 29·07 Mn. 29·36	198 221 Incr. 23	23·44	33·4	208

These results give a rate of increase of loss per degree of temperature which, arbitrarily assuming that it may be referred wholly to the saturation deficit, amounts very closely to the following, viz. :—

$$\text{Loss in grammes per } 1^\circ \text{ C.} = -4{\cdot}5 + 0{\cdot}955\,\zeta,$$

this formula giving

1·34, 9·57, and 23·53 instead of 1·33, 9·68, and 23·44.

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* The saturation-deficit measures the capacity of a given volume of air mixed with aqueous vapour to absorb further aqueous vapour; the temperature measures the activity of the molecular motion leading to absorption.

The temperature range being small is, however, not very satisfactory, although the results are determined from a considerable number of means.

If we take the results for absolute dryness in Table V., we get a second degree curve and by no means identical results. Combining the two series, however, which though not quite satisfactory is probably better than depending wholly on either, we obtain the following results :—

Table VII.

Mean Temp. Group ...	20·0	21·8	23·5	25·9	29·4	33·4	35·6
Absolute Dryness	6·13	8·59	13·55	14·74	22·55	29·36	34·65
Loss for 1° C.	1·33	3·90	5·80	9·68	15·90	23·44	22·00
Calculated, as below ...	1·81	3·78	7·75	8·70	14·95	20·40	24·63

If these be assumed to be of equal weight, the linear equation which will represent them as well as any other may be obtained by the method of least squares. This solution gives the coefficient 0·793 instead of 0·955. Adopting 0·8 as sufficiently accurate, we obtain the calculated results in line 4 in Table VII. above, that is again arbitrarily assuming it to be independent of absolute temperature ; that is to say,

$$\text{Loss in grammes for } 1^\circ \text{ C.} = -3{\cdot}09 + 0{\cdot}8\,\zeta.$$

In such results, however, it must be remembered that we are not justified in assuming that the effect is not due in part to increase of absolute temperature, and theoretical considerations indicate that both temperature and saturation deficit (or absolute dryness) influence the result.

12. *Deduction of Formula for Total Loss.*

The examination thus far would appear to indicate that we may perhaps be able to interpret the data by assuming that the loss is either the sum, or else the product of two linear terms, one representing the losses due to temperature, the other those due to dryness. Into these alternatives we now inquire.

It may be noted that though into saturated air of the same temperature as the skin, or of a higher temperature, there could be no evaporation from the skin, yet there would still be a loss from the lungs. Ordinarily, therefore, we must not have $E=0$ for either $\zeta=0$, or $T=0$. Hence, if in (17) we put

$$\phi_1(\mathfrak{T})=A(1+\alpha\mathfrak{T})\ ; \quad \text{and} \quad \phi_2(\zeta)=B(1+\beta\zeta)$$

as probably sufficiently representative, we shall have, writing C for AB,

$$\phi_1(\mathfrak{T})\phi_2(\zeta)=C\{1+\alpha\mathfrak{T}+\beta\zeta+\alpha\beta\mathfrak{T}\zeta\}. \quad . \quad . \quad . \quad (18)$$

If α and β were sufficiently small, the terms in $\mathfrak{T}\zeta$ may either be negligible or, within restricted limits, may be compensated by adjusting the values of C, α, and β. It might therefore, with sufficient approximation, be possible at least for any small range of results, to satisfy the observations with an equation of the form

$$E=a+bT+c\zeta, \quad . \quad . \quad . \quad . \quad (19)$$

or even with

$$E=a'+b'T\zeta\ ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (19\,a)$$

or yet again it may be necessary to introduce in (19) a third term, viz., $d\,.\,T\zeta$.

Solving first by the method of least squares, the whole of the observations in Table I. for losses from W. A. O. weight 68 kilogrammes, not affected by wind, we obtain

$$E=-33{\cdot}6+2{\cdot}93\,T+4{\cdot}77\zeta.$$

This gives the values shown in column (8) of Table I. These values, however, it will be seen systematically deviate from the data, and show that the formula (19) cannot satisfactorily represent the results. Analysing the data from another point of view, we have from Tables V. and VI., giving group means, the following results :—

Table VIII.

	Obsd. loss.	Calc. loss.	Diff. Obsd. − Calc.
122·6 …………	60	61	−1
187·3 …………	81	72	+9
318·4 …………	86	93	−7
331·8 …………	95·5	104	−8·5
663·0 …………	157	150	+7
980·6 …………	208	203	+5
1233·6 …………	241	245	−4

The equation which gives the calculated results, found by the method of least squares, is

$$E = 40\cdot39 + 0\cdot166\,T\zeta.$$

When the intrinsic discrepancies are considered (see Table I.), this result is eminently satisfactory. Hence, taking the total group and solving the system of 26 equations by the method of least squares, for a' and b' in (19 a) we obtain

$$E = 43\cdot8 + 0\cdot154\,T\zeta. \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

The results are shown in column (9) of Table I., and agree remarkably well with the observed results, and may be taken as generally representing them. Thus with the present data formula (19 a) may be regarded as quite satisfactory for the aggregate loss.

13. *Losses of Water and Carbon Dioxide.*

In order that a mass such as the human body shall maintain a sensibly uniform temperature, its thermogenesis and thermolysis must be in continuous adjustment with external changes of temperature and with other conditions affecting the rate of loss of heat energy by convection, by radiation, and by evaporation, etc. The physical conditions are such that it can be anticipated *à priori*, on grounds indicated by Professor Osborne, that variations will be exhibited more markedly in what may be called the external losses, than in what may be called the internal losses, and particularly than in the loss of water and carbon dioxide from the lungs and respiratory apparatus. The latter, indeed, shows a remarkable constancy as regards both temperature and dryness, and it may be pointed out that in the results, for subjects weighing respectively 68 and 46 kilograms, the weight appeared to be without influence. While this, of course, is accidental, it discloses the fact that the lung losses must not be assumed to stand in any constant relation to the weight.

The following table shows the results tabulated in the order of temperature (p. 348) :—

TABLE IX.

Obsn. No.	Temp. C.	Absolute Dryness.	Grammes. Lung Water expired.	Grammes. CO_2 expired.	Weight.
1	15·0	4·23	16·24	22·3	68
2	17·0	4·67	14·7	22·1	46
3	17·3	4·96	14·5	21·82	68
4	17·5	4·87	15·6	24·14	68
5	18·9	6·04	14·4	19·9	68
*6	19·0	8·70	17·8	22·32	68
*7	19·3	6·65	14·9	22·75	68
8	20·2	7·53	14·2	23·63	68
	Mean 18·02	Mean 5·96	Mean 15·29	Mean 22·38	
9	20·2	8·32	13·9	18·75	68
10	21·0	9·48	13·4	18·36	68
11	21·1	5·40	13·3	22·56	68
*12	21·1	11·54	14·87	21·75	68
13	21·7	9·99	14·7	21·26	68
*14	21·7	13·15	17·5	23·78	68
15	22·5	6·74	13·5	21·07	68
16	22·8	10·12	13·1	23·0	46
	Mean 21·51	Mean 9·35	Mean 14·28	Mean 21·32	
17	23·3	14·33	......	......	68
18	23·9	13·86	16 0	22·7	68
19	23·9	16·18	17·2	22·45	46
20	25·0	16·45	16·1	22·8	68
21	26·1	14·31	14·0	21·39	68
22	27·0	15·70	15·5	23·99	68
24	27·2	13·06	15·0	25·47	68
25	27·2	18·00	15·8	21·17	68
27	29·2	21·90	14·9	22·37	68
	Mean 24·94	Mean 16·18	Mean 15·56	Mean 22·79	
28	30·5	23·76	......	......	46
29	31·7	28·53	20·0	24·38	68
*30	32·8	27·97	18·2	21·85	68
*31	33·6	31·14	16·85	21·29	68
34	35·7	34·57	15·4	25·0	46
*35	35·8	34·39	17·1	25·05	68
37	37·0	37·99	21·8	28·96	68
39	38·3	40·29	18·5	25·36	46
	Mean 34·99	Mean 33·55	Mean 18·26	Mean 24·56	
Mean	of whole 24·86	15·70	15·77	22·70	

* Observations taken when wind velocity was not inconsiderable.

These results show no definite progression, and hence group means are taken (see Table). With these four means we have the following results, viz.:—

TABLE X.

Temp.	H_2O Obsd.	H_2O Calc.	CO_2.	CO_2 Calc.	Ratio H_2O/CO_2.
18·02	15·29	14·65	22·38	21·83	0·683
21·51	14·28	14·96	21·32	22·07	0·670
24·94	15·56	15·63	22·79	22·59	0·683
34·99	18·26	18·19	24·56	24·55	0·743
					Mean 0·695

It is desirable, if possible, to use the argument $T\zeta$ again, and an examination of the results discloses the fact that this argument is to be preferred. In this way we find from the above data, by the least-square method in grammes, that the loss of water E_h from the lungs is

$$E_h = 14{\cdot}29 + 0{\cdot}00332\, T\zeta, \quad . \quad . \quad . \quad . \quad (21)$$

T being expressed in degrees centigrade and ζ in millimetres pressure.

Similarly we find for the loss E_d of carbon dioxide

$$E_d = 21{\cdot}56 + 0{\cdot}00255\, T\zeta. \quad . \quad . \quad . \quad . \quad (22)$$

The average ratio of the loss of water from the lungs to the loss of carbon dioxide is 0·695 for the ranges in temperature and dryness of the experiment, but is of course a function of these, if (21) and (22) represent the actual fact. The actual loss of carbon would therefore be 3/11 of the above, viz.,

$$E_c = 5{\cdot}88 + 0{\cdot}0007\, T\zeta. \quad . \quad . \quad . \quad . \quad (23)$$

It would thus appear that we could have one expression to include both E_h and E_c, viz., E_l, that is,

$$E_l = E_h + E_c = 20{\cdot}17 + 0{\cdot}004\, T\zeta. \quad . \quad . \quad . \quad (24)$$

It is questionable, however, whether either of these expressions (21) and (23) holds after a temperature of say 31° C. is reached, when heat accumulation sets up physiologically labile conditions, viz., conditions whereby the organic adjustment of the thermolytic and thermomagnetic equilibrium is so disturbed as to be no longer capable of re-establishment.

14. *General indications for further investigation.*

From what has preceded, it will be seen that the aggregate loss may be supposed to be made up in the following way :—

Skin Losses. Evaporation of Water, &c., from Skin. H_2O.	Losses from Respiratory System. CO_2 and H_2O.	
Argument (i.) Temperature ($\mathfrak{T}$ or T).	Arg. (i.) Temperature.	Arg. (i.) Dryness.
(ii.) Dryness (ζ)	(ii.) Dryness.	(ii.) Temperature.
(iii.) Wind velocity (V)	(iii.) Physical condition.	(iii.) Other physical conditions.
(iv.) Other physical conditions (θ).	(iv.) Physiological conditions.	(iv.) Physiological conditions.
(v.) Physiological conditions (ψ).		
(vi.) Weight of body (W).		

Consequently, writing θ for other unspecified physical conditions and ψ for physiological conditions, the formula for total loss should, theoretically at least, take the form :

$$E = A \,.\, \phi_1(\mathfrak{T}, \zeta, V, W) + C\phi_2(\mathfrak{T}, \zeta, \theta, \psi, W) + H\phi_3(W, \zeta, \mathfrak{T}, \theta, \psi), \qquad (25)$$

$$\text{that is} \qquad E = E_s \quad + E_c \qquad\qquad + E_h$$

E_s denoting evaporation through the skin. Probably this expression also should be a function of θ and ψ.

The data presented in Professor Osborne's paper do not permit, so far, an accurate determination of a formula for the various losses. Suggestions are consequently made in the light of the mathematical examination of the results already furnished, as to what would appear to be essential.

In order to quantitatively dissect the physiological from the physical elements, in order, for example, to ascertain how the rate of loss is influenced by conditions or by habit of body (or by health, race, skin colour, adpiosity, &c.), it is essential to reduce the uncertainties connected with the purely external or purely physical condition to a minimum. This will necessitate several things, viz. :

(i.) The adequate control and the exact measurement of the physical conditions of the experiments (in regard, for example, to temperature, humidity, air movement, and possibly other elements (*e. g.* electrical conditions, ionization of air, etc.).

(ii.) The securing a sufficient range of variation in these conditions to determine accurately the form of the mathematical function representing them.

(iii.) A sufficient number of experiments to establish an average condition or a series of average conditions corresponding to such variations as sex, colour, race, etc. (norms for sex, etc.).

(iv.) And thus the measure of the variation from any norm or series of norms is ascertained.

With such material available the study of special cases and the determination of special physiological data will become possible, though obviously the undertaking is a considerable one. The magnitude of the various numbers and the degree of uncertainty indicate that probably 20-minute observations would be ample, instead of 60-minute ones.

With regard to special conditions, it may be remarked that the data should include both mean and extreme conditions, and are especially important where any physiologically labile condition supervenes. It is only with a series of properly deduced norms that the meaning of individual departures therefrom can be unequivocally traced, and the magnitude of the discrepancy of individual results as shown in the preceding tabulations of the data are a sufficient proof of this.

The suggested establishment of norms, for the purpose of critically studying individual or group deviations therefrom, evidently requires that physical conditions shall range through the following, viz., measurement of losses :—

(i.) (*a*) In still air, (*b*) air in medium, and (*c*) in rapid movement, each with three widely different degrees of dryness.

(ii.) (*a*) Air of low temperature, (*b*) medium, and (*c*) high temperature, each with great diversity of dryness.

(iii.) A special series at very low temperatures.

(iv.) A special series ranging from say 30° to 45° C., viz., in the range where the labile conditions occur in still air, and with medium and high wind velocity.

Finally, it may be observed that if, as appears to be the case, all the losses can be put in the form $a + b\mathrm{T}\zeta$ with sufficient approximation (except at critical temperatures, etc.): then for the empirical representation of results or for small corrections for given ranges that expression is of practical value.

XXXI. *Studies in the Photometry of Lights of Different Colours.—II. Spectral Luminosity Curves by the Method of Critical Frequency.* By HERBERT E. IVES [*].

THE first paper of this series [†] described spectral luminosity curves obtained by the equality of brightness photometer and the flicker photometer. It was found that these curves change differently in response to variations in illumination ; the equality of brightness method exhibits the Purkinje effect, the flicker method an opposite and hitherto unobserved shift. At high illuminations the distribution of brightness in the spectrum is closely the same by the two methods, at low illuminations quite different. With the standard of comparison used—the unsaturated yellow of a standard carbon incandescent lamp—the two kinds of luminosity curves are usually of somewhat different areas at their nearest approach to similarity in shape. The differences between the two kinds of curves and the changes in each due to changed illumination are less with small fields than with large.

The present paper describes certain spectral luminosity curves obtained with the same apparatus and conditions as before but by the method of critical frequency (sometimes called "persistence of vision") [‡]. These were studied primarily with the expectation of obtaining some light on the peculiarities of the flicker method, with which the critical frequency method is presumably closely allied. Certain seeming disagreements in the results of other observers furnished a starting point for the work here described. Stuhr, for instance, found that the method of critical frequency gave results identical to those of the flicker photometer. But Haycraft [§] obtained, by critical frequency measurements on the spectrum, a pronounced Purkinje shift. Since, according to the writer's experiments, the flicker photometer gives a reversed Purkinje effect, it would follow that this identity of the results of the two methods cannot hold for all illuminations. Allen [*] has obtained "persistence of vision curves" showing a greater sensibility to pure flicker in the peripheral retina as compared with the fovea or central retina. On the other hand, the flicker photometer has been found by the writer to be less sensitive when the peripheral retina is used.

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[*] Communicated by the Author.

[†] Phil. Mag. July 1912, p. 149.

[‡] For details of each of the four methods of photometry discussed in these papers—equality of brightness, flicker, critical frequency, and visual acuity—reference should be made to the first communication.

[§] Journ. of Physiology, vol. xxi. pp. 126–146.

The present investigation for the most part clears up these seeming discrepancies. Most of the results of other observers have been confirmed. Their divergence is shown to be due to different experimental conditions.

The procedure for obtaining the luminosity curves was similar to that described in the previous paper. The largest field ($5^\circ\cdot 2 \times 8^\circ\cdot 6$) was used most of the time, because with it the Purkinje and similar effects are most marked. First a set of flicker and of equality of brightness measurements was made as in the previous work. Then the spectral light was extinguished and the speed was determined at which flicker vanished when the rapidly rotating white disk was illuminated by the comparison lamp alone. The various spectral regions were then substituted for the comparison lamp, and the slit widths were determined which would cause flicker to disappear at the speed found for the comparison lamp. With critical frequency settings the mean of appearing and disappearing flicker was taken. Ten readings for each illumination were usually made, and between each set the eye was rested about a minute in the faint light of the photometer room. In this manner three kinds of spectral luminosity curves were found at each illumination. The first measurements were made at two illuminations, a medium and a low, namely 50 I. U. and 5 I. U. The results are given in fig. 1, curves B and C. (Later a variation in the procedure was found preferable as will be noted and the curves A, B, and C (fig. 1) were made by this more satisfactory method.)

It appears from these curves that the flicker and the critical frequency method both show the reversed Purkinje effect, in contrast to the regular Purkinje shift with the equality of brightness method. It appears too that the areas of the three kinds of curves differ.

The occurrence of the reversed Purkinje shift by the critical frequency method is in apparent contradiction to the work of Haycraft. It claimed first attention. For purposes of comparison Haycraft's results are reproduced in

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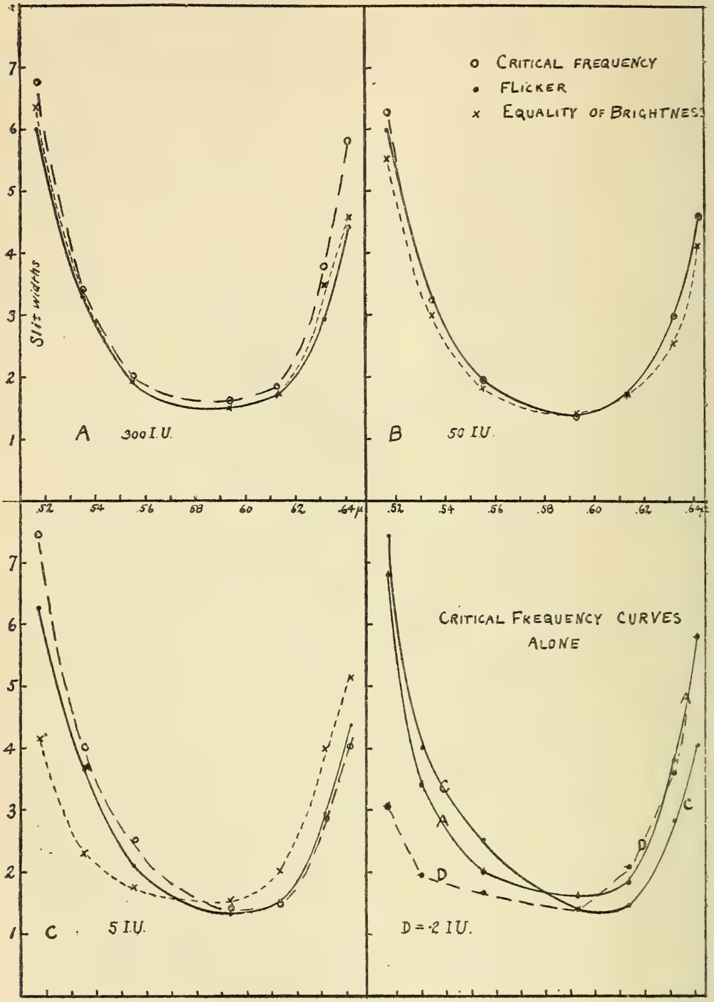
[*] Phys. Rev. vol. xi. p. 257; vol. xxviii. p. 45.

Fig. 1.



Inverse Luminosity Curves by Critical Frequency, Equality of Brightness, and Flicker Methods.

fig. 2 *. In his work Haycraft adopts a different procedure from that of the writer. The illumination is not kept constant throughout the spectrum, but is taken as it naturally occurs, consequently the ends are always much darker than

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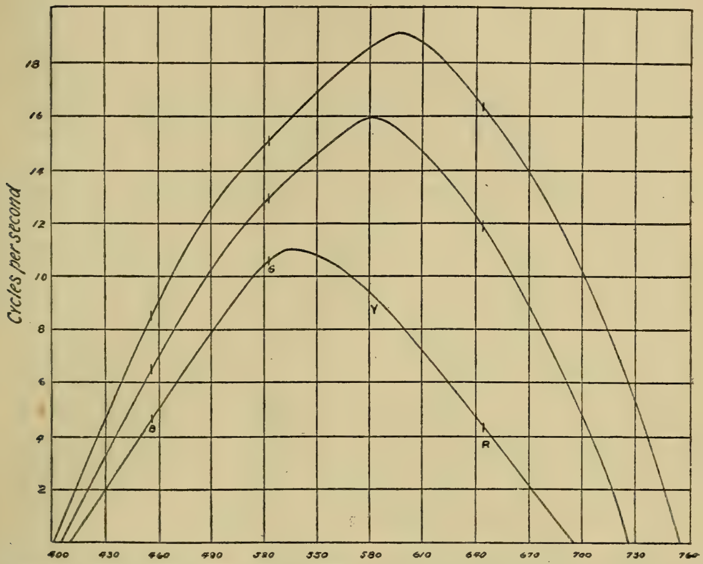
* Haycraft, *loc. cit.*

the middle. He plots critical frequencies for constant slit-width, instead of slit-widths or reciprocal slit-widths for constant frequency as is here done. It is in this difference of procedure that we find the explanation of the difference between Haycraft's results and those of the present writer. An examination of Haycraft's curves indicates that in all cases the end portions of the spectrum are at illuminations calling for lower critical speeds than the low curve obtained by the writer. Curve C, fig. 1, corresponds to 18 cycles per second, while Haycraft's speeds vary from 19 to about 4 cycles per second. After noting this fact an additional critical frequency curve (Curve D) was determined for an illumination less than a tenth that of Curve C. This shows, with respect to the one at 5 I. U., a pronounced Purkinje shift, in qualitative agreement with Haycraft.

Fig. 2.

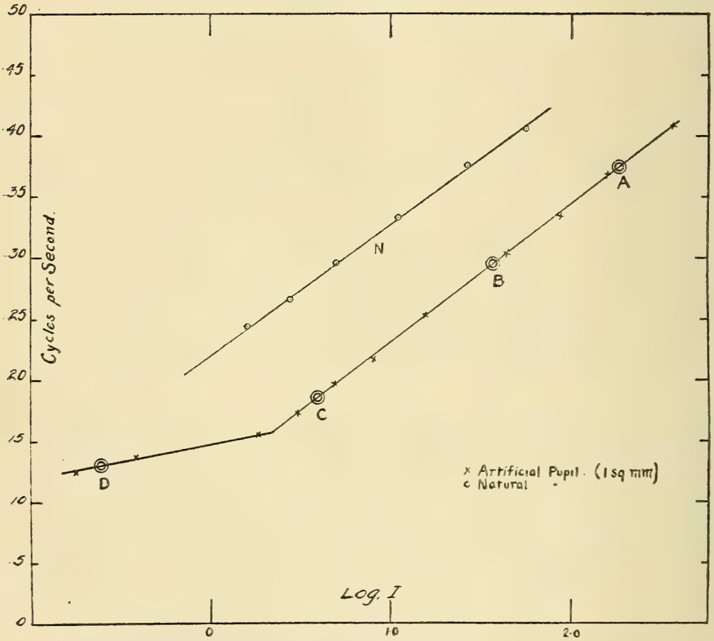


Critical Frequencies of the spectral colours at high, medium, and low intensities, showing relatively greater change for red (R). After *Haycraft.*

Apparently, therefore, the changes which accompany decreasing illumination are first in one direction and then in the other. In searching for some other phenomena of critical frequency with which this might be coordinated, it occurred to the writer that the regions of the Purkinje and the reversed Purkinje effect might be connected with the two different logarithmic rates at which critical frequency varies with illumination. Porter * has found for white light that the relationship $n=k\ \log. \mathrm{I}+p$ represents the critical frequency phenomena, where $n=$ critical frequency in cycles per second, I= illumination, k and p are constants. The constant k has, however, two different values, one below ·25 M.C., another above that illumination. When plotted on semilogarithmic paper this relation is shown by two straight lines of different inclination meeting at ·25 M.C. It has been surmised that this illumination represents the point of change from cone to rod vision.

Fig. 3 gives the results of a determination of these

Fig. 3.



Critical Frequency-Illumination Relations for "White" Light.

straight lines with the author's apparatus for the "white" light of the standard carbon lamp. The abscissæ are logarithms of illumination units (metre candles on magnesium oxide surface, viewed through artificial pupil of 1 sq. mm.) † ;

* Proc. Roy. Soc. lxxix. p. 313 (1902).

† The illumination is that given by the intensity of the light source divided by the square of the distance. The illumination upon the retina, when the disk is in motion, corresponds to a steady illumination of half the plotted values.

the ordinates are critical frequencies in cycles per second. The three circles B, C, and D show the illuminations at which the three critical frequency luminosity curves were obtained. The reversed Purkinje effect occurs in the upper or "cone" region, the Purkinje effect in the lower or "rod" region. In Haycraft's work the ends of the spectrum were always in the "rod" region, so that the reversed Purkinje effect would show itself only as a warping of the medium illumination parts of the curves by an amount easily to be mistaken for errors of measurement.

Before leaving consideration of fig. 3 attention is called to curve N. This was made without the artificial pupil of 1 sq. mm. aperture. It furnishes a means of evaluating the "illumination units" here used, in terms of metre candles illumination of the standard white magnesium oxide surface. To reduce illumination units to metre candles it is necessary to divide by from 7 to 8 over the range of these experiments. This figure of course applies to the writer's eye, and will be different for other eyes in proportion to the relative natural pupillary apertures of different observers. Since in working with critical frequencies the field is illuminated for only one half the time, the flicker and equality of brightness illumination units should be doubled in order to use this diagram.

While the discovery of the relation of the Purkinje effect and its opposite to the two regions previously found by Porter is a distinct step, further insight into the phenomena follows from more detailed study. On examination of this data it is obvious that the facts presented point to different critical frequency-illumination relations for different colours. Moreover, the relation in the rod region must be different from that in the cone region, the change taking place at about 2·5 I. U.

To test this hypothesis a set of critical frequency determinations was made for various spectral colours. Illuminations were reduced by neutral tint screens * placed over the spectroscope slit. The results shown in fig. 4 bear out the surmise. In the "cone" region the different colours give straight lines (to within the errors of measurement) which are differently inclined in such manner as to give the reversed Purkinje effect. At critical frequencies of from 18–12 cycles per second these lines change their directions. Their new relative inclinations are such as to give the true Purkinje effect. The most remarkable

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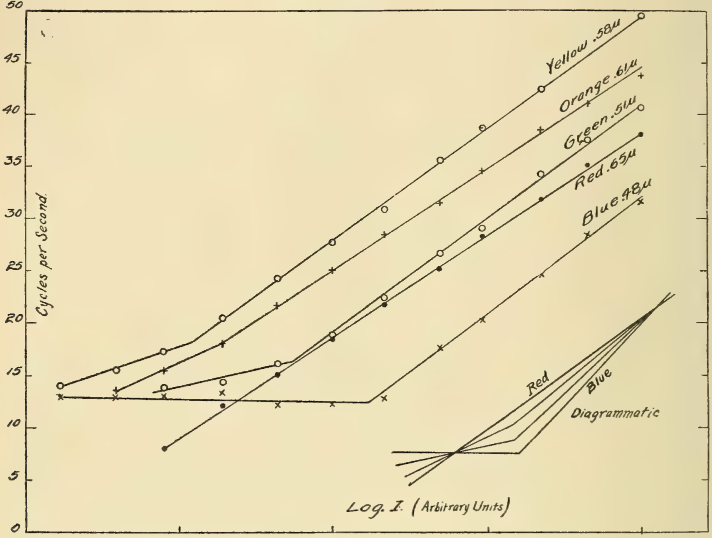
* "A Form of Neutral Tint Screen," Herbert E. Ives & M. Luckiesh, Phys. Review, May 1911.

curves are those for deep red (·650 μ) and for blue (·480 μ). The red curve maintains its direction. The blue curve changes from a diagonal to a horizontal line; that is, the critical frequency becomes a constant, independent of illumination. The behaviour of the other colours is intermediate.

Fig. 4.



Critical Frequency-Illumination Relations for Different Colours.

A simple relationship therefore exists between the luminosity curves at different illuminations, as given by this method. In the region above the change of direction we have, if S_λ is the slit-width at λ, F the critical frequency, $F = K_\lambda \log S_\lambda + P_\lambda$, where K_λ is a constant involving the relation between critical frequency and intensity of radiation for the individual eye for the colour in question and for the size of the photometric field, and where P_λ is a constant involving the quantity of energy emitted by the source and the dispersion and dimensions of the instrument of observation, as well as the relative sensibility of the observer's eye to flicker at different colours at a given speed. In short, the law found by Porter holds for different colours if the values of the constants are changed in the equation expressing the law. Upon determining the inverse luminosity curve or slit-width curve for any chosen critical frequency, knowledge of the constants K_λ enables one at once to construct the corresponding curves for any other critical frequency. This may be done graphically, by determining the straight lines of fig. 4 and plotting them in such units that at certain critical frequencies the values of Log. I are the logarithms of the experimentally determined slit-widths. The slit-widths for any other critical frequency (and hence illumination, by reference to the line given by the standard light source) may be read off the plot by laying a straight edge parallel to the axis of abscissæ at the desired critical frequency.

From the standpoint of the present investigation the chief interest in the study of the method of critical frequencies lies in the light it throws on the flicker photometer. For the sensibility of the method is too low for it to claim a place in accurate photometry, a matter which is discussed later. Does any simple relation similar to that just found, exist between the flicker photometer luminosity curves at different illuminations? A number of similarities between the critical frequency and the flicker photometer curves point to their close relationship. They both show the reversed Purkinje effect. The luminosity curves are at least approximately alike. Moreover, a peculiarity of the low illumination flicker curves given in the last paper, which apparently was an anomaly, is in accordance with the critical frequency phenomena. The point referred to is this: in the curve for the lowest illumination at which it was found practicable to work with the flicker photometer, the red side starts to decrease in brightness—that is, to give a Purkinje shift—while the blue side is still decreasing, thus resulting in a narrowing of the curve. Examination of the critical frequency plots of figs 3 and 4 shows that the bend in the "white" curve occurs at a higher illumination (or critical frequency) than for blue, and at a lower illumination than for orange and red. Consequently, if the white light curve be taken as a reference standard, the change of relative direction, constituting the shift from the reversed to the true Purkinje effect, occurs sooner for red than for green or blue, precisely what was observed.

Can the flicker photometer be considered merely as a device for equating two flicker sensations which are dovetailed one into the other? The similarities just considered would suggest this possibility. We may consider two ways by which this equating could take place. Either the illumination determines the relative quantities of light which measure equal; or else the speed at which the flicker photometer is run in order to make the colour alternation just disappear determines these quantities. Both factors may play a part, and others may enter as well.

Let us consider the measurement of spectral colours against one taken as the standard of illumination, or against a white. On the critical frequency-log. I diagram, the standard and the colours to be measured are each represented by straight lines. At a given illumination a quantity of any coloured radiation may be chosen such that flicker will disappear with it at the same speed as with a chosen standard. If the rise and fall or the contour of the flicker sensation is independent of the speed or changes in the same manner for all colours with change of speed, then this coloured light may be alternated with the standard, and the speed may be reduced to the point where colour flicker is just about to appear—forming a flicker photometer. The speed not altering the equality of the two contours, the relative quantities of the standard light and the coloured will be the same as was required to make flicker disappear with each separately at the critical frequency for the standard. If this is the state of affairs the same relationship between critical frequency and slit widths exists for both standard and colour in the flicker method as with the method of critical frequency. That is

$$F = K_s \log I + p_s,$$

$$F = K_\lambda \log S_\lambda + p_\lambda.$$

We may then substitute for the critical frequency in question its value in terms of the standard illumination, and obtain as a result

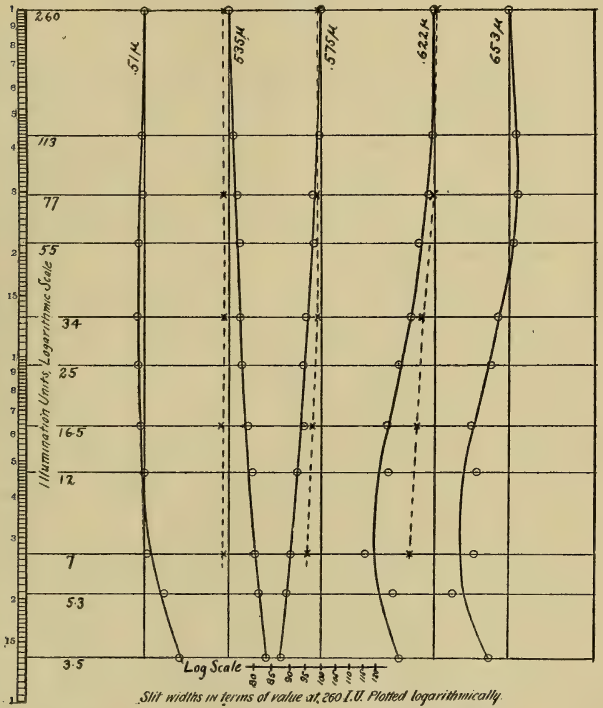
$$K_s \log I + C = K_\lambda \log S_\lambda,$$

that is, the logarithms of the slit-widths will plot as a straight line against the logarithms of the illuminations.

On the second assumption the relative quantities of the standard and the coloured radiation would be read off the diagram (fig. 4) for the speed at which the flicker photometer is run. The possibility is, however, practically ruled out by the fact that, as shown by reference to the data of the first paper, the flicker photometer speeds for an illumination showing a strong reversed Purkinje effect are 8 to 10 cycles per second; therefore, from the data in the present paper they are well down in the Purkinje region. Speed cannot therefore be the dominant factor.

Considerable time and care have been spent in testing the first possibility. The data in the previous paper were plotted in the form of $\dfrac{\log S_\lambda}{\log S_{\cdot 575\,\mu}}$ against log I. The resultant lines were so nearly straight as to raise expectations that the law of the flicker photometer had been found. To obtain a more conclusive test, isochromatics were then made. The spectral colour and the standard were matched by the flicker photometer at a series of illuminations, stepping down by means of carefully calibrated neutral tint screens. On plotting the logarithms of the slit-widths * against the logarithms of the illumination, the curves of fig. 5 were obtained. These are not straight lines. The simple law anticipated does not hold. However, the effect of change of illumination is shown in a manner which indicates the method of study by isochromatics to be an excellent one for following the course

Fig. 5.



Isochromatics, showing variation in relative brightness of spectral colours due to variation of illumination, Flicker Photometer.

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* For greater certainty slit-widths were not used in this case. Instead the voltage of the test lamp was altered, the intensity change being first determined for each colour by a spectro-photometer in which a variable sector disk took the place of the usual variable slit.

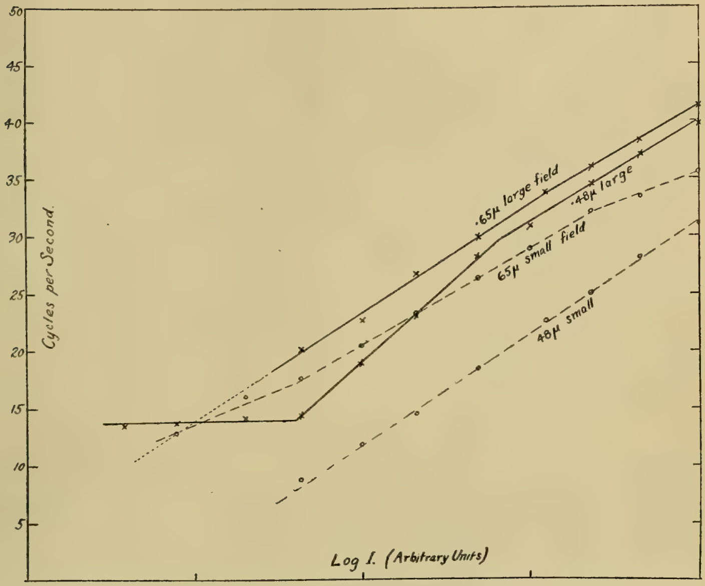
of the Purkinje and similar phenomena. It shows the rationale of changes which might, if obtained by another method, be considered within experimental errors.

The curves show the reversed Purkinje effect, making clear that the phenomena of the method of critical frequency dominate in the flicker photometer. But instead of the expected straight lines the nearest approach to them lies in the long, rather flat curves of the middle of the spectrum, while at the red and blue ends a double curvature indicates a marked deviation at high illumination from the form to be expected.

Two possible explanations of these deviations claim attention. First, that the critical frequency phenomena when plotted logarithmically are not really straight lines, but curves, and that the flicker method actually agrees with the other, but by reason of the greater accuracy of the method shows the curvature clearly. Second, that while the critical frequency phenomena are true straight lines as plotted logarithmically, the flicker phenomena are merely similar and not identical.

The first explanation is not improbable, at least for the medium and low illuminations. The deviations from straightness are probably within the errors of measurement by the critical frequency method. (The log scale of fig. 5 is many times larger than that of figs. 3 and 4.) The lowest inflexion point of the red curves corresponds fairly well to the illumination at which this should occur according to fig. 3. At higher illuminations the flicker photometer results would be explained if the separate critical frequency curves showed a tendency to bend to the horizontal, the blue showing the greatest tendency, the red the least, with white lying between. Fig. 6 shows red and blue curves, each the mean of several sets in which the eye was rested in total darkness for several minutes between each set of readings. Under these conditions the higher illuminations produce strong complementary after-images. These curves do exhibit the bending suggested and also much more for blue than for red. It may probably be explained as a fatigue or contrast effect. However, an extended series of such measurements showed that the occurrence of the change in direction is somewhat dependent on the condition of the eye, and is not nearly so easy to observe with white as with coloured light. It is also probably dependent on the character of the photometric field. The small bright area of the prism face surrounded by an entirely black field may be expected to cause contrast and induction phenomena which would be absent under less extreme conditions. It may be much more marked under the doubled illumination which holds when two colours are matched in the flicker photometer.

Fig. 6.



Critical Frequency-Illumination Relations for large and small Photometric Fields.

If the latter supposition is correct it virtually means the adoption of the second explanation, namely that the critical frequency phenomena probably follow the straight line relationship, and that the flicker photometer, influenced by various factors, merely follows this relationship closely but not exactly. In fig. 1, curve A, taken at a higher illumination than those previously mentioned, the critical frequency curve shows a larger shift toward blue than does the flicker, while in curve C the shift toward red is greater. Both these differences are near the limit of accuracy of the measurements, but are consistent in indicating that the flicker photometer method does not follow the critical frequency method absolutely. On the whole it appears more probable that the critical frequency phenomena do obey the simple law given above and that the flicker photometer phenomena merely approximate thereto. Other factors, such as speed, mutual action of different colours, perhaps the influence of the surrounding field, enter in the latter case to cause deviations from the simple conditions. At any rate the simple law which it was hoped to find does not hold for the flicker photometer.

The actual effect of this deviation from the simple law is to cause apparent constancy of the flicker curve at moderately high illuminations, since the changes over a long range of intensities are of nearly the order of the error of reading. It must not be forgotten too that these data are all for a large photometric field. Data for a small field are given in fig. 5 by the dotted lines. Their much greater constancy of value is noticeable.

A similar test of the method of equality of brightness was made by plotting both the writer's data and Kœnig's in terms of log I against log. slit-width, and some isochromatics were tried. Here again long curves were obtained. If any simple law holds with regard to these phenomena it is not this logarithmic relation, which, it may be noted, is of course merely Fechner's law.

Small Photometric Fields.

Fig. 6 shows red and blue critical frequency data for a small photometric field (diameter 1°·9). The effect of reducing the field size is to swing the blue line around nearer parallel with the red, which is swung but little. The reversed Purkinje effect will therefore be less, a condition similar to that produced in the flicker photometer by the same change of field size.

The most interesting point shown in the figure, however, is the behaviour of the blue at very low illuminations. The violent change of direction which occurs with a large field either is absent or is pushed down to a lower illumination than here tried. The fovea behaves toward blue light just as the larger area of the retina behaves toward red. This is in line with the finding of Kœnig that the fovea is blue-blind. It is here found to be not strictly blue-blind but blind to the gray sensation which replaces blue at low illuminations for a larger or peripheral field. There is also some indication that the red small field curve tends to turn at low illuminations in somewhat the manner of the blue curve for large fields. The bearing of these points on colour vision is discussed shortly.

An outstanding difference between Haycraft's work and the present research may be noted here. While his results are qualitatively explained by the data of fig. 4, these data would not give his curves. Blue light attains a fixed critical frequency of about 12 cycles per second, while Haycraft worked as low as 4 or 5 cycles per second. The explanation may be sought in two facts : his work was done with the eye in an extreme condition of dark adaptation brought on by one hour's rest in the dark before observations, and a very small photometric field was used. That the constant frequency attained by blue light depends upon the condition of the eye is shown by the different values in figs. 4 and 5, while the work on small fields shows that the turning point may be depressed by restricting the area of the retina. The combination of these two factors is probably sufficient to explain the different values of critical speeds at which the same phenomena occur in the two investigations. Peculiarities of the individual eyes, such as differences in the relative proportions of rods and cones, might also be of influence.

Sensibility of the Critical Frequency Method.

Photometry by the method of critical frequency is considerably less accurate than by either the equality of brightness or the flicker method. From among the sets of readings made near the close of the investigation one day's observations on "white" light were selected at random and studied with the following result : At a high illumination, corresponding to 43 cycles per second, the average deviation from the mean of twenty settings was 1·8 per cent. in speed ; at 32 cycles per second, 1·9 per cent. in speed ; at 23 cycles, 1·9 per cent. in speed. These errors appear small, but when expressed in terms of brightness instead of speed they are found to be too large for accurate photometry. They correspond respectively to 18 per cent., 14 per cent., and 10 per cent. in brightness, or five or ten times the mean error by the flicker method. Settings made on different days, or on the same day with the fatigued and unfatigued eye, are apt to differ by two to three per cent. in speed.

The critical frequency method is highly subject to disturbances whose explanation is physiological or psychological. Depending on whether the eye has been rested in diffused light, in darkness, or by blindfolding, the absolute values of the readings will be increased or decreased throughout the spectrum *. Some experiments made during the period covered by this investigation indicate that these changes may affect an unsaturated colour more than a saturated one, or less. This would cause the area of the luminosity curve to be in error.

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* F. Allen, Phys. Rev. 1900 & 1909, *loc. cit.*

The slopes of the straight lines, obtained by plotting, as in fig. 3, are subject to variations, in general of such a nature as would be caused by variations in the size of the field, indicating a changing balance between rods and cones. A rather curious difference in the setting depends on whether the variable be speed or brightness. If the slit-width for any colour is held constant the critical speed may be found by several settings. If this speed is held and the brightness varied by changing the slit till flicker vanishes, the value obtained from settings for slit-width may differ as much as 15 or 20 per cent. from the previously fixed value, an effect apparently acting one way at one period and another way at another. This disturbance affects all the spectral colours to the same extent (as nearly as can be judged) so that a curve of larger or smaller area results depending on the method of setting.

In view of this fact the critical frequency curves of fig. 1, curves A to D were made by speed settings alone (except D). First the critical speed for the standard lamp illumination was determined ; then, with the slit set at the value given by the previous flicker photometer setting, the critical speed for the colour was determined. From the log I–critical speed relations previously determined the equivalent change in slit-width was read off. The relative values for the different colours, that is the shape of the curves and the Purkinje shift, were as previously obtained by the procedure described above, but these curves are given as being freer from objection.

Great care is taken in the present paper to draw only such conclusions as are warranted by the accuracy of the method.

The Areas of the Curves.

Because of the small sensibility of the critical frequency method and its susceptibility to obscure disturbing factors, it is hard to draw very definite conclusions from the difference of area shown between certain of the critical frequency curves and the flicker and equality of brightness curves. Suffice to say that such differences are apt to occur and that the previously found differences of area between the flicker and equality of brightness curves again appear *. These are sufficient to show the futility of concluding that different photometric methods give identical results simply because they show the same distribution of brightness in the spectrum. The capacity of different methods to summate will form the subject of a subsequent paper.

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* In fig. 1, curves A, the equality of brightness area is smaller than the flicker, a condition not previously found at this illumination

Peripheral versus Central Vision.

The greater sensibility of the peripheral retina to motion and to flicker has been frequently observed. In the work on the flicker photometer the possibility of using this greater peripheral sensitiveness was investigated, with the unexpected result of finding a smaller sensitiveness than for central or foveal vision. During the course of the present work frequent comparisons were made between central and peripheral sensitiveness to flicker, with different colours, and with large and small fields, at different illuminations. The findings explain satisfactorily the failure of peripheral vision with the flicker photometer.

The most significant fact was learned on the failure of several attempts to secure the critical frequency-illumination relationship by peripheral vision settings, namely, that such greater sensitiveness as the periphery possesses quickly disappears on continued gazing. It is, at least at medium and at high illuminations, merely a momentary phenomenon, not at all available for careful and continued photometric settings. The periphery, by the fatigue due to steady use, becomes for the long wave end of the spectrum, and at high illuminations, less sensitive than the centre of the retina. The fovea alone appears to have properties sufficiently constant and dependable for photometric use.

After this fact was established qualitative observations were carried out, with the eye thoroughly rested between observations. The critical speed for central vision was established, the eye was directed so that the image fell about 7° from the fovea, usually on the nasal side, and the direction of change of speed necessary to produce or destroy flicker was noted. These observations showed that for very high, nearly dazzling illumination, there is little choice between centre and periphery with red and blue light, with large or small field. A large retinal field is always more sensitive than a small one, apparently a pure area effect.

At lower illuminations the periphery becomes more and more sensitive to blue flicker, but less to red flicker. At very low illuminations (about 12 cycles per second) with a small field the difference between the behaviour of the two colours is enormous. By direct vision a blue field is almost invisible and flicker is perceived only at a low speed ; by peripheral vision the field flashes out brilliantly, and simultaneously a flicker of large amplitude appears. For red light these conditions are reversed; it is now the periphery which is less sensitive to light and flicker. This behaviour of red and blue light at low illuminations has been previously noted by Dow[*].

Bearing upon Theories of Colour Vision.

Kœnig in his study of the visual purple found its absorption spectrum to correspond to the luminosity of the spectrum at very low illumination, *i.e.*, twilight or colourless vision[†]. The product of its decomposition, the visual yellow (which is in turn decomposed) has an absorption spectrum corresponding to the distribution of the blue sensation at high illuminations. Study of the red, green, and blue sensation curves with continually decreasing illumination[‡] shows that the colourless sensation at low illuminations arises by gradual transformation of the blue sensation—the red and green retaining their distribution substantially unaltered. At high illuminations, therefore, gray or white is a mixture of three colour sensations (using the word sensation in Kœnig's meaning), while at low illuminations the gray sensation is a simple one due to the transformed blue remaining after the red and green has dropped below the threshold. At high illuminations Kœnig considers the visual purple to be broken down successively into visual yellow and the final colourless product; at low illuminations only the first transformation takes place. Visual purple occurs only in the retinal rods, and is absent from the cones, consequently from the fovea. The fovea he finds is blue-blind.

In the first paper of this series it was suggested that the retinal cones or colour-seeing organs might be responsible for the behaviour of the flicker photometer. It was assumed that the peripheral cones, which are large, might be more red-sensitive; that is, more extreme in their cone character than the foveal cones. Situated among the rods, their exaggerated red-sensitiveness might with decreasing illumination tend to partly counterbalance the increasing part played by the rods. In the flicker photometer these cones acting alone (due in some way to the intermittent stimulus) produce the reversed Purkinje effect. Could the rods be made to act alone, an abnormally large Purkinje effect would result.

[*] Phil. Mag. Jan. 1910, p. 58.

[†] "Ueber den Menschlichen Sehpurpur," *Gesammelte Abhandlungen*, p. 338.

[‡] E. Tonn, *Zeit. f. Psych. u. Phys.* vi. p. 279 (1894).

In the equality of brightness photometer (corresponding to ordinary vision) the rods and cones act together, the former prevailing at low illuminations.

The new facts learned in the present investigation seem to be in accord with the work of Kœnig and this suggested mode of action of the flicker photometer. We must add to the hypothesis, just reviewed, the assumption that the blue sensation, although produced in the visual purple of the rods, behaves in a similar manner to the red and green sensation localized in the cones. It is not necessary to assume an exaggerated sensitiveness in the peripheral rods because the greater number of rods will alone account for that. We have then at high illuminations colour vision, and response to intermittent stimuli as represented by the logarithmic relation discussed above. This state is due to cone action and visual yellow decomposition. At a certain low illumination we cease abruptly to have blue vision. In its stead we have colourless vision obeying an entirely different law with respect to flicker and ascribable to the incomplete breakdown of visual purple. In accordance with this hypothesis is the fact that the violent change of direction in the blue line of the log I–critical frequency diagram, is coincident with the change in appearance from blue to gray. Also the observation, in confirmation of the statement of Kœnig and others, that red light does not change to gray but continues red until the lowest illumination possible to make observations. The different behaviour of blue light for a small or a large field at low illumination is also in accord with the anatomical fact that the rods are missing in the fovea, and with Kœnig's observation of foveal blue blindness.

Summary.

1. Spectral luminosity curves obtained by the method of critical frequency show a reversed Purkinje effect, but at very low illuminations a true Purkinje effect, the latter observed by Haycraft.

2. A plot of critical frequencies against the logarithm of the illumination for white light gives, as found by Porter, two straight lines of different slope, which meet at about 2·5 I.U. The reversed Purkinje effect occurs above this point, the true Purkinje effect below it.

3. When separate colours are investigated and plotted in the above manner, a set of straight lines of differing slope results.

4. At about 2·5 I.U. these lines in general change their

slope, but while the line for deep red does not change, that for blue becomes horizontal, or critical frequency becomes independent of illumination. The Purkinje effect and its opposite follow at once from these facts.

5. The flicker photometer is shown to be largely influenced by the critical frequency phenomena, but not to obey the simple law which would follow were it a mere dove-tailing of two pure flickers.

6. The peripheral retina is found to be more sensitive to flicker only for momentary observation before adaptation or fatigue sets in. The fovea is more sensitive to red flicker, the periphery to blue, and the difference is more striking at low illuminations, as noticed by Dow.

7. The phenomena of critical frequency are in general accord with Kœnig's theory of the function of the visual purple and with the hypothesis that the retinal cones are chiefly active in the case of intermittent or alternating stimuli.

Physical Laboratory,
National Electric Lamp Association,
Cleveland, Ohio.
January, 1912.

XXXII. *On the Diffusion of Actinium Emanation and the Active Deposit produced by it.* *By* Prof. J. C. McLennan[*].

IN a paper by W. T. Kennedy, published in the Phil. Mag. of November 1909, an account is given of some experiments on the active deposit products of actinium.

In one series of experiments observations were made on the distribution of the active deposit obtained on two parallel plates, 2 mm. apart and charged to 250 volts, the actinium salt being so placed immediately below the plates that the emanation from it was compelled to diffuse up between them. In these experiments the plates and the salt were inserted in a vessel in which the air could be maintained at any selected pressure, and the observations were made on the distribution of the active deposit obtained on the plates with air-pressures of 760 mm., 120 mm., 25 mm., and 5 mm. respectively. The distributions of the deposit obtained at atmospheric pressure on the negatively charged plate, and also on the positively charged one, are shown in fig. 1. From the curves it will be seen that on both the positively charged plate and on the negative one the active deposit was greatest close to the salt, and was distributed in gradually decreasing amounts at points on the plates farther and farther from the salt. The curves given in the paper for the distributions corresponding to the other pressures were of the same general character. It was found, however, that while at atmospheric pressure by far the greater part of the active deposit was found on the negatively charged plate, at the other pressures investigated the deposit on the positively charged plate became relatively greater, and at 5 mm. was almost identical in amount with that obtained on the negative plate.

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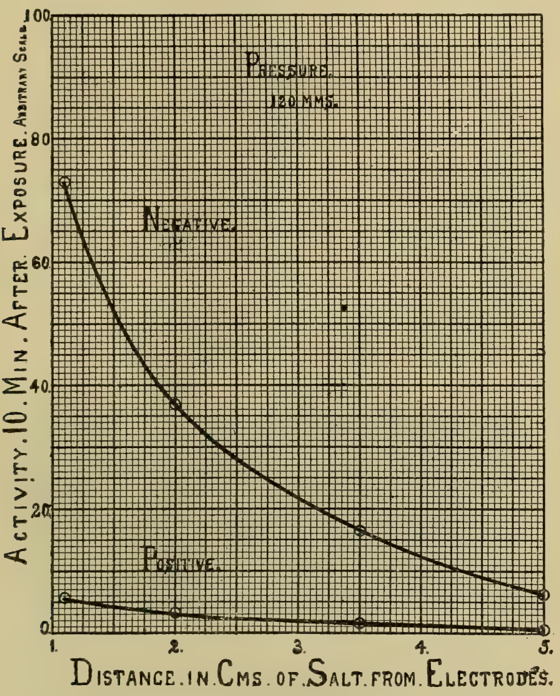
[*] Communicated by the Author. Presented to the Royal Society of Canada, May 17, 1912.

Fig. 1.

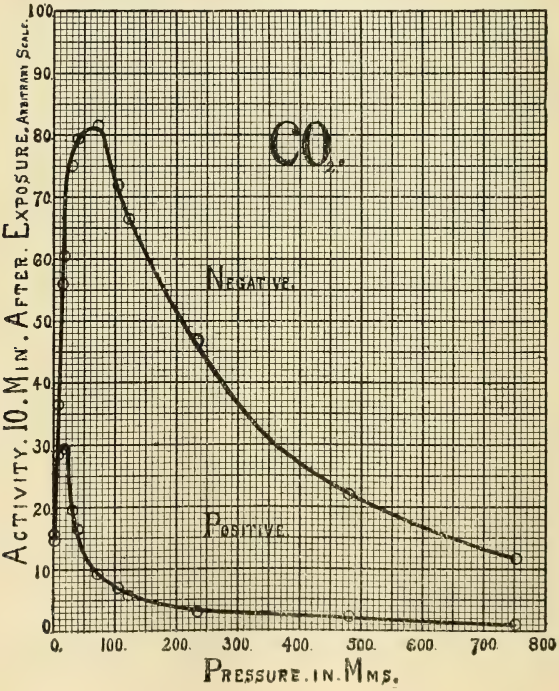


In a second series of experiments observations were made on the amount of deposit obtained on the plates at a point 2·5 cm. above the salt, when the pressure of the air in the vessel in which the plates and salt were placed was gradually diminished. The results for this set of observations are given in Table I., and the curves representing them are shown in fig. 2.

TABLE I.

Pressure.	Activity on the Cathode.	Activity on the Anode.
·5 mm.	11·7	11·3
1·0 ,,	14·5	14·0
2·0 ,,	18·5	17·0
7·5 ,,	37·5	29·0
12·0 ,,	49·0	33·0
25·0 ,,	62·5	28·5
42·0 ,,	82·3	17·7
72·0 ,,	92·0	10·0
92·0 ,,	91·0	7·5
120·0 ,,	76·0	5·5
135·0 ,,	73·0	5·0
162·0 ,,	68·0	4·0
192·0 ,,	66·5	3·0
320·0 ,,	43·0	1·15
500·0 ,,	31·0	·70
750·0 ,,	20·5	·45

Fig. 2.



From these curves it will be seen that a maximum deposit was obtained on the negative plate at the point under observation at a pressure of approximately 80 mm., while the maximum deposit on the positive plate was not obtained until a pressure of 16 mm. was reached.

When these experiments were repeated with carbon dioxide and with hydrogen in place of air it was found that the maximum deposit at the same point on the negative plate was obtained with a pressure of 60 mm. in carbon dioxide, and with a pressure of 250 mm. in hydrogen.

Further, in some additional observations made by Kennedy, since the publication of the paper referred to above, it was found on measuring the deposit on the negative plate at different points at various distances from the salt that a simple law existed connecting the pressure corresponding to the maximum deposit obtained at a given observation point with the distance of that point from the salt. According to this law, if x_1 represents the distance from the salt of the point at which the deposit was investigated, and p_1 the pressure which gave a maximum deposit at that point, then p_1 was found to vary inversely with x_1, or

$$p_1 x_1 = \text{a constant}\,^*.$$

In seeking an interpretation of these results it seems clear from the first set of observations that the maximum deposits found in the second series of observations were not due to the presence in the space between the plates of a maximum concentration of either the emanation from the salt, or of the active deposit particles produced by the emanation, but that they arose from the fact that the emanation from actinium was an exceedingly short-lived radioactive product. On account of this characteristic the emanation at higher pressures, such as atmospheric, was wholly transformed before it diffused very far from the salt, and but little of it therefore reached the point on the plates under observation in the experiments illustrated by the curve in fig. 2. With decreasing pressures, however, the emanation diffused more and more rapidly, and the effect of this produced at first an increase in the concentration of the emanation at the point of observation. With the pressures decreased still further the emanation diffused more and more rapidly, and finally at the lowest pressure obtainable the diffusion became so rapid that the concentration at the point of observation became exceedingly small. With this explanation it follows that the amount of

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[*] Trans. Brit. Assoc. 1910, p. 543.

active deposit obtainable at any selected point should pass through a maximum value if exposures were made as the pressure was lowered. It is evident, too, from the interpretation given that the pressure corresponding to the maximum deposit at a selected point should be the lower the farther the point under observation on the plates was taken from the salt.

In considering these experiments it can be readily seen that the law observed by Kennedy, viz.

$$p_1 x_1 = \text{a constant},$$

throws some additional light on the manner in which the active deposit particles become positively charged.

Let P denote the concentration of the emanation between the plates and

K_1 its coefficient of diffusion.

Taking the axis of x along a line midway between the plates and perpendicular to the salt, it follows that $-K_1 \frac{dP}{dx}$ is the rate at which the emanation crosses a square centimetre taken perpendicular to the axis.

From this it can be readily seen that $K_1 \frac{d^2P}{dx^2}$ represents the rate at which the emanation increases per c.c. at a distance x from the salt.

If now λ_1 is the decay constant of the emanation, $\lambda_1 P$ will denote the rate at which the emanation in each cubic centimetre is being transformed into the active deposit product, and therefore for equilibrium we have

$$K_1 \frac{d^2P}{dx^2} = \lambda_1 P,$$

or

$$\frac{d^2P}{dx^2} = \frac{\lambda_1 P}{K_1},$$

or

$$P = c_1 e^{-\sqrt{\frac{\lambda_1}{K_1}} x} + c_2 e^{\sqrt{\frac{\lambda_1}{K_1}} x}.$$

If, now, when $x=0$, $P=P_0$, and when

$x = \text{infinity}$, $P=0$,

we have $C_2 = 0$,

and $C_1 = P_0$,

or

$$P = P_0 e^{-\sqrt{\frac{\lambda_1}{K_1}} \cdot x}.$$

Again, if q be the rate at which the emanation is leaving the salt per sq. cm., we have

$$q = -K_1 \frac{dP}{dx} \text{ when } x = 0;$$

and since $$\frac{dP}{dx} = -\sqrt{\frac{\lambda_1}{K_1}}\, P_0 e^{-\sqrt{\frac{\lambda_1}{K_1}} . x},$$

$$q = \sqrt{K_1\lambda_1}\, P_0, \quad \text{or} \quad P_0 = \frac{q}{\sqrt{K_1\lambda_1}},$$

$$\therefore \; P = \frac{q}{\sqrt{K_1\lambda_1}} e^{-\sqrt{\frac{\lambda_1}{K_1}} . x}.$$

If, now, we assume that the same law governs the diffusion of the emanation which holds for a small quantity of one gas diffusing into a second we may take

$$K_1 = \frac{A_1}{p},$$

where p is the pressure of the gas in which the diffusion takes place and A_1 is a constant.

We have then

$$P = q \frac{\sqrt{p}}{\sqrt{A_1\lambda_1}} e^{-\sqrt{\frac{\lambda_1 p}{A_1}} . x}.$$

In order to find the pressure corresponding to a maximum deposit for a selected value of x it suffices to apply the condition

$$\frac{dP}{dp} = 0.$$

This gives $$\frac{1}{\sqrt{p}} - \sqrt{\frac{\lambda_1}{A_1}}\, x = 0,$$

or $$p = \frac{A_1}{\lambda_1 x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

i. e. the pressure corresponding to the maximum deposit at a point at a distance x from the salt should, with the assumptions made above, be inversely proportional to the square of the distance of the point under observation from the surface of the salt. This result, it will be seen, is distinctly at variance with the law of distribution discovered by Kennedy.

If, however, we assume that K, the coefficient of diffusion of the emanation, varies inversely as the square of the pressure of the gas into which it is diffusing, *i. e.*, that

$$K_1 = A'/p^2,$$

then we have

$$P = \frac{q}{\sqrt{A_1\lambda_1}}\, p e^{-p\sqrt{\frac{\lambda_1}{A_1}}\,x}\,;$$

and with the condition of maximum deposit $\frac{dP}{dp} = 0$ applied we have

$$p\sqrt{\frac{\lambda_1}{A_1}}\,x = 1,$$

or

$$p = \sqrt{\frac{A_1}{\lambda_1}}\,\frac{1}{x}, \quad \ldots\ldots \quad (2)$$

which is the law observed by Kennedy.

There seems no sufficient reason, however, for assuming the inverse square law for the coefficient of diffusion of the emanation, and it would seem, therefore, that we must look elsewhere for an explanation of the discrepancy.

In the argument presented above we have tacitly assumed (1) that q, the rate at which the emanation leaves the salt, is the same for all pressures, and (2) that a direct proportionality exists between the concentration of the positively charged active deposit particles and the concentration of the emanation, for all pressures of the gas in which the emanation is diffusing.

If the active deposit particles became positively charged directly in the process of their creation from the emanation, then such an assumption as the latter might be warrantable. If, however, these deposit particles gain their charge from the ions produced in the gas by the radiation emitted by the emanation in the process of transformation (as would seem to be true from the results of Schmidt *), then a factor depending on the pressure of the gas should be introduced into the relation connecting the concentration of the emanation and that of the positively charged active deposit particles at any point. For the concentration of the emanation at a distance x from the salt, assuming $K_1 = A_1/p$, we have, as shown above,

$$P = \frac{q\sqrt{p}}{\sqrt{\lambda_1 A_1}}\, e^{-\sqrt{\frac{\lambda_1}{A_1}}\,p\,.\,x}.$$

Let now D be the concentration at the same point of the positively charged active deposit particles, and assume $D=\alpha P$, where α is some function of the pressure p.

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* *Phys. Zeit.* 9 Jahr. No. 6, p. 184, 1908.

We have then

$$D=\frac{\alpha q\sqrt{p}}{\sqrt{A_1\lambda_1}}e^{-\sqrt{\frac{\lambda_1}{A_1}}px};$$

or if $$\alpha q=y,$$

then $$D=y\frac{\sqrt{p}}{\sqrt{A_1\lambda_1}}e^{-\sqrt{\frac{\lambda_1}{A_1}}px}.$$

For the pressure corresponding to the maximum cathodic deposit

$$\frac{dD}{dp}=0,$$

and this gives

$$\frac{1}{y}\frac{dy}{dp}+\frac{1}{2p}-\frac{1}{2}\frac{1}{p^{\frac{1}{2}}}\sqrt{\frac{\lambda_1}{A_1}}=0. \quad . \quad . \quad . \quad (3)$$

According to Kennedy's results, we have also the relation

$$px=c, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and combining equations (3) and (4) we have

$$\frac{1}{y}\frac{dy}{dp}+\frac{1}{2p}-\frac{1}{2}\frac{c}{p^{\frac{3}{2}}}\sqrt{\frac{\lambda_1}{A_1}}=0;$$

i. e., $$\log y+\tfrac{1}{2}\log p+\frac{c}{p^{\frac{1}{2}}}\sqrt{\frac{\lambda_1}{A_1}}=c_1,$$

or $$\log yp^{\frac{1}{2}}=-\frac{a}{p^{\frac{1}{2}}}+c_1 \text{ where } a=c\sqrt{\frac{\lambda_1}{A_1}}.$$

From this $$yp^{\frac{1}{2}}=e^{-a/p^{\frac{1}{2}}+c_1},$$

$$=A_2e^{-a/p^{\frac{1}{2}}}, \quad \text{where } A_2=e^{c_1},$$

or $$y=\frac{A_2}{p^{\frac{1}{2}}}e^{-a/p^{\frac{1}{2}}}.$$

Now from the form of the function constituting the right-hand member of this equation we see that y vanishes both for very high and for very low values of p. It follows then on resubstituting for y that the product of αq is given by

$$\alpha q = \frac{A}{p^{\frac{1}{2}}} e^{-a/p^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where q is the rate at which the emanation leaves the salt, and α is the proportionality factor between the concentration of the emanation and the concentration of the active deposit particles produced from it, which are or become positively charged.

It is evident, then, from (5) that the law discovered by Kennedy for the distribution of the active deposit leads to the conclusion that either one or other of the magnitudes α and q, or perhaps both, is a function of the pressure.

Some interesting information, which could be used in testing the result given in (5), might readily be obtained by confining the actinium salt and the emanation liberated from it at different pressures in a small chamber constructed in such a way that a negatively charged electrode inserted in it would have access to all the emanation during an exposure.

Such an arrangement, however, would possess one defect. According to the conclusions we have reached, the active deposit particles which get positively charged would grow fewer and fewer as the pressure in the chamber was lowered, and the quantity of the deposit which would reach the negatively charged electrode through the agency of the directive action of its field would then become less and less with decreasing pressures. On the other hand, as the pressure was decreased the active deposit particles, which were uncharged, would reach the bounding surface of the chamber, including the surface of the negatively charged electrode, either by projection or diffusion in ever-increasing amounts; and so, unless the negatively charged electrode had a surface exceedingly small in comparison with that of the walls of the chamber, the deposits obtained on it at different pressures could not be taken as measures of the number of active deposit particles present which carried a positive charge.

Some information might also be obtained regarding α and q separately by arranging suitable experiments with an active emanation possessing a longer life than that from actinium—for example, that from radium.

If a quantity of radium salt were confined in a chamber to which a second was attached which could be cooled down with liquid air, the emanation expelled by the salt in a given time could be collected in the second chamber. This could be done for a series of different pressures, care being taken to see that the condensation was carried on for periods sufficiently long to eliminate differences in the rate of diffusion of the emanation from the first chamber to the second. Measurements made on the amount of emanation obtained in the second chamber would then give information directly about q, the rate at which the emanation from radium left the salt at different pressures.

To obtain information about the factor α it would suffice to make repeated exposures of a negatively charged electrode of small surface to equal quantities of radium emanation, at a number of different pressures. The experimental arrangements outlined in the preceding paragraph would probably suffice to enable one to repeatedly obtain in the second chamber a definite amount of emanation. These repeated condensations could be made at a very low air-pressure and then, if the second or condensation chamber were cut off from the first and air afterwards admitted into it to any selected pressure, it could be used as the exposure chamber as well. This would enable one to find how the number of positively charged active deposit particles from a given amount of radium emanation varied with the pressure of the air in which the emanation was diffusing.

If α and q were found separately in this way with the emanation from radium, one could see whether or not their product varied in accordance with such a law as that represented by (5), and from the resulting agreement or lack of it one could come to some definite conclusion regarding the validity of the explanation offered in the present communication of the results obtained by Kennedy.

If the law enunciated in (5) were confirmed by the experiments just described the result would go to show that active deposit particles at the instant of their creation are uncharged, and that the positive charge usually found on them when diffusing in gases at ordinary pressures is acquired from the surrounding ionized gas at a stage later than that of their creation.

The experiments begun by Kennedy are being conducted in the direction indicated above, and it is expected that results will be obtained shortly which may enable one to settle definitely the origin of the charges acquired by the active deposit particles.

Physical Laboratory,
University of Toronto,
May 1, 1912.

XXXIII. *The Photo-Electric Effect of some Compounds.* *By* A. Ll. Hughes, *D.Sc.*, *B.A.*, *Research Scholar of Emmanuel College, Cambridge*[*].

MOST of our knowledge of the photo-electric effect has been derived from experiments on metallic surfaces. Comparatively few experiments have been carried out on surfaces of salts and other compounds. Some early experiments were carried out on compounds (chiefly salts) by Knoblauch[†]. Stark[‡] investigated the photo-electric effect of a number of organic substances. Byk and Borck[§] studied the photo-electric effect of solid anthracene. In a paper[‖], which deals mainly with an attempt to find ionization by ultra-violet light in vapours containing photo-electric elements, a few experiments are described on the photo-electric effect of certain solid compounds. It was concluded that the surfaces prepared by dipping a metal plate into a molten salt and allowing a layer to solidify on the plate were very unsatisfactory. As the photo-electrons come from a depth of only a few molecules, it is essential that the outermost surface layer should be chemically identical with the interior, if we are to consider that we are studying the real photo-electric effect of any particular salt. The most satisfactory way of preparing a pure surface of any salt or other compound is to distil it in a liquid air vacuum. The surface layers may then be considered to be chemically identical with the rest of the deposit. To investigate such surfaces, I used the apparatus with which I measured the emission velocities of photo-electrons from surfaces of metals prepared by distillation *in vacuo*[¶]. The experiments showed that it required more energy to liberate an electron from an electronegative element like arsenic or selenium, than from metals. If a metal be in combination with an electronegative element, then more work will be required to liberate the electron from the molecule than from the uncombined metallic atom. It was thought that quantitative measurements of the emission velocities of photo-electrons from salts would furnish very useful information regarding the work necessary to liberate an electron from the molecules of different compounds. Such results, if they could be obtained, would be of the utmost value in forming an electrical theory of chemical affinity. The investigation, however, indicates the fact that salts have no real photo-electric effect of their own, and that the effect of the light is first, to decompose the salt, and secondly, to cause an emission of electrons from the metallic element which is left.

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[*] Communicated by Sir J. J. Thomson, O.M., F.R.S.

[†] Knoblauch, *Zeit. f. Phys. Chemie*, xxix. p. 527 (1899).

[‡] Stark, *Phys. Zeits.* ix. pp. 481, 661 (1908).

[§] Byk & Borck, *Verh. d. D. Phys. Ges.* p. 621 (1910).

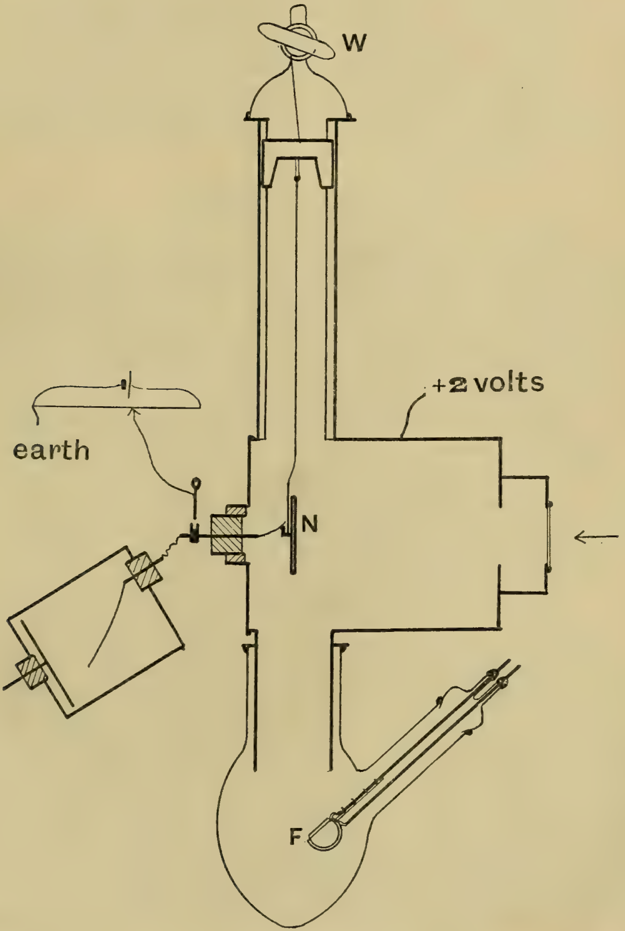
[‖] Hughes, Proc. Camb. Phil. Soc. xvi. p. 375 (1911).

[¶] Hughes, Phil. Trans. (A), vol. ccxii. p. 205 (1912).

The Apparatus.

The apparatus used is shown in fig. 1. A more detailed description is given in my paper on the emission velocities of photo-electrons. The nickel disk N can be raised up or down by means of the winch W. When in the position shown,

Fig. 1.



the emission of electrons from the surface of the disk can be investigated. When it is desired to cover the disk with a layer of distilled salt, the disk is lowered until it is near the furnace F. The furnace consists of two quartz bowls, one of which fits into the other. Between the two bowls is a broad strip of Pt or Ni foil which can be heated to redness by an electric current. The substance to be distilled is placed inside the smaller quartz bowl. The distillation is effected in a liquid air vacuum, and the disk, when covered with a suitable layer of the distilled substance, is raised into position where it is exposed to the light. The pressure of the residual gases never exceeds ·001 mm. during the process of distillation.

The source of ultra-violet light was a mercury arc in quartz glass, the shortest wave-length emitted by this lamp being λ1849*. The lamp was always placed at a distance of 30 cm. from the apparatus.

Experimental Results.

These results were usually obtained with an accelerating potential of +2 volts on the case. Certain tests, described later, were used when it was suspected that the conductivity of the substance was so small that its surface became charged, and therefore at a different potential from that of the disk. Except in the case of BaO, the conductivity of the salts was good enough to enable the experiments to be carried out without any trouble of this kind. The leak on the first exposure to the light was measured in as short a time as possible, since the magnitude of the effect grows with the time of exposure. An appreciable time, however, is required to determine the rate at which the gold leaf of the electroscope moves, and hence it is that the time during which the leak was measured could not be reduced below about 20 or 30 seconds. In the following table, for example, the leak on the first exposure was obtained by observing the rate of motion of the gold leaf during the first 40 seconds. (In the second table, the leak during the first minute's exposure was measured in three parts and the growth of the effect is clearly shown.) The leak was again measured over a period of 30 seconds at the end of 5 minutes' exposure to the light. The surface was then shielded from the light for 5 minutes, and the leak was once more measured when the light was directed on to the surface at the end of that period. The unit of photo-electric leak throughout the paper is the same, being approximately 10^{-15} amp. The sign $<$ indicates that there was no leak, and the number which follows gives the leak which could have been detected.

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* Hughes, Proc. Camb. Phil. Soc. xvi. p. 428 (1912).

Mercurous Iodide.

	Leak.
First exposure. (First 40 secs.)	= 11
Exposed 5 mins.	48
In dark 5 ,, ...	36
Exposed 5 ,, ...	69
In dark 25 ,, ...	71
Exposed 3 ,, ...	85
Exposed 15 ,, ...	110
In dark 15 ,, ...	103
Exposed 7 ,, ...	170

Mercuric Iodide.

		Leak.
First exposures ..	First 20 secs.	= 7·2
	Next 20 ,,	11·8
	Next 15 ,,	17·7
In dark 5 mins.		21·1
Exposed 3 ,, ...		63
Exposed 3 ,, ...		87
In dark 9 ,, ...		80
Exposed 3 ,, ...		120

Mercurous Chloride.

		Leak.
First exposures ..	< First 20 secs.	= <·7
	Next 60 ,,	3·5
	Next 60 ,,	5·7
Exposed 5 mins.		26·4
Exposed 5 ,, ...		40·5
In dark 6 ,, ...		40·5
In dark 10 ,, ...		35·0
Exposed 4 ,, ...		53·7
Exposed 6 ,, ...		70·4

Another layer was distilled but was not exposed to the light until 15 hours later. The effect in the first 20 seconds was < 1. As before, the leak increased on exposure of the surface to the light. This experiment shows that the increase in the leak depends upon the exposure to the light and not on the age of the surface.

Mercuric Chloride.

		Leak.
First exposures ..	First 60 secs.	=<·6
	Next 120 ,,	4·5
	Next 120 ,,	8·0
Exposed 3 mins.		14·5
Exposed 30 ,,		88·0
In dark 19 hrs.		144·0
Exposed 5 mins.		100·0
Exposed 40 ,,		122·0

Bismuth Trichloride.

	Leak.
First exposure	= 10·7
Exposed 2 mins.	20
Exposed 5 ,,	45
In dark 8 ,,	49
Exposed 8 ,,	62
Exposed 20 ,,	93

It will be noticed that, generally speaking, the effect of keeping the surface in the dark is to reduce the leak at the next exposure, or, if this be not effected, to reduce the rate at which the leak increases.

Antimony Tri-iodide.

This salt differed from the others in that it started with a big leak, and that prolonged exposure to light caused a reduction in this leak.

	Leak.
First exposure	=110
Exposed 6 mins.	143
Exposed 14 ,,	80
Exposed 20 ,,	55
In dark 90 ,,	82

Lead Iodide.

No leak was obtained from lead iodide in the first experiments. The results of long exposure to light with the other salts suggested a further investigation of the effect of prolonged exposure on lead iodide.

	Leak.
First exposure	=<·2
Exposed 3 mins.	2·8
Exposed 5 ,,	4·5
Exposed 40 ,,	12·7
Exposed 70 ,,	16·2

The effect with lead iodide is much smaller than with the other salts and requires a longer exposure to produce it.

Ferric Chloride.

	Leak.
First exposure	< ·2
Exposed 15 mins.	·9
Exposed 20 ,,	1·0

Another layer was distilled and kept in the dark for 1½ hours. On being exposed to the ultra-violet light for the first time, the leak was < ·2, as before.

In view of the results of some experiments on deliquescent compounds, described later, the effect of admitting moist air for two hours was tried. It was then pumped out and a high vacuum was obtained by the liquid air method. The photo-electric leak was practically the same as before, being 1·2; after 40 mins. exposure it rose to 1·5. While the surfaces of the $ZnCl_2$ and P_2O_5 retained a moist appearance after contact with air, the ferric chloride surface became quite dry again in the liquid air vacuum. This is probably the reason why there is no appreciable increase in the leak. It is known that the hydrates of ferric chloride have a vapour pressure, and consequently the salt will part with its water of crystallization in a vacuum.

Zinc Chloride.

	Leak.
First exposure	< ·2
Exposed 1 hour	< ·2
Exposed 1 ,,	< ·2

This shows that a dry surface of zinc chloride is not photo-electric. Air from the room, not dried in any way, was admitted for 5 minutes at atmospheric pressure and then pumped out again. The surface did not appear to be wet as far as one could judge from the appearance of the deposit on the disk when viewed through the glass portion of the apparatus.

After admitting air	160
Exposed 5 mins.	240
Exposed 5 ,,	255

Moist air was then passed into the apparatus and pumped out as before. The surface now appeared to be almost liquid.

After admitting moist air	250
In dark 5 mins.	300
Exposed 5 ,,	340

Phosphorus Pentoxide.

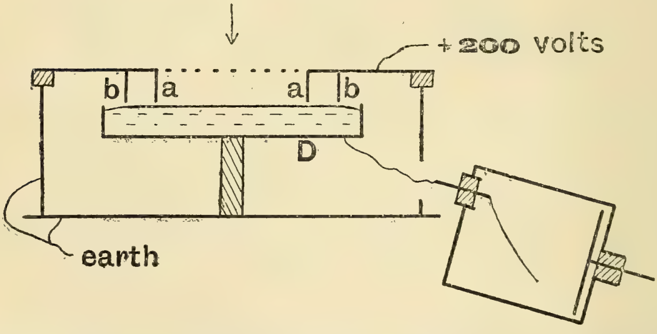
A very thin transparent layer of P_2O_5 was sublimed on to the nickel plate. It was exposed to the light for two hours, yet the leak, if it existed, was always less than ·1. On admitting atmospheric air at 1 cm. pressure and pumping out immediately, the leak went up to 4. Air at 760 mm., from the room, was admitted several times. The biggest leak obtained after such treatment was 70. Similar effects were obtained when the deposit of P_2O_5 was thick enough to be opaque.

It is difficult to see why the $ZnCl_2$ and P_2O_5, which are not photo-electric in themselves, become so when in combination with water. Water, according to Brillouin [*], does not emit electricity when exposed to ultra-violet light. The act of solution in water can hardly be regarded as causing the liberation of a photo-electric element in any way analogous to the surface decomposition of a mercury salt by ultra-violet light. In the case of the phosphorus pentoxide and water, not one of the elements involved has been shown to be photo-electric when illuminated by the light from a mercury lamp.

Water.

The arrangement shown in fig. 2 was devised to test the photo-electric properties of water. The water was contained in a shallow dish (the lid of a circular tin). The two rings of brass *a* and *b* were arranged as shown to prevent stray light reaching the edges of the dish, since the metal has an enormous photo-electric effect compared with compounds in general. The rings *a* and *b* and the top-piece to which they were soldered were covered with soot. Between the edges of the rings *a* and *b* and the surface of the water, there was a

Fig. 2.



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[*] Sir J. J. Thomson, 'Conduct. of Elec. through Gases,' p. 289.

clearance of 1 or 2 mm. With different samples of distilled water, leaks of from 5 to 15 units were obtained. In this case, owing to the bigger aperture and the fact that the lamp could be placed closer to it, the amount of light which fell on the surface of the water was 7 or 8 times greater than that which fell on the surfaces of the salts.

The variations in the leak seem to indicate that the leak is more likely due to some spurious effect than to a real effect with the pure water. It is impossible, with this simple arrangement, to obtain the same clearance between the rings and the water surface time after time. Hence, the amount of stray light which gets to the edges of the dish may vary to a great extent. It is also possible that slight traces of impurities in the water may give rise to photo-electric effects. To prove that water is not photo-electric to a higher degree of accuracy than was obtained in these experiments would require more elaborate experimental arrangements. However, it seems clearly established that the photo-electric properties of the water in the surfaces of the moist $ZnCl_2$ and P_2O_5 are quite inadequate to account for the big emission of electricity from these surfaces. The effect seems to depend, in some way, on the combination of the water with the $ZnCl_2$ and the P_2O_5.

Anthracene.

Stark * found that anthracene vapour could be ionized by means of the light from a mercury lamp. Anthracene has also been shown to be photoelectric when in the solid state. Anthracene is one of the few organic compounds suitable for experiments on the emission velocities of its photo-electrons, since it has no appreciable vapour pressure at ordinary temperatures to interfere with the velocity measurements. The total leak from the anthracene surface was much larger than that from any of the compounds previously used, being of the order 10^3 units. When illuminated by the unresolved light from the mercury arc, the anthracene charged up to a potential of ·87 volt. The great photo-electric sensitiveness of anthracene enabled one to study its effect with isolated wave-lengths. There was not the slightest trace of any effect with wave-lengths longer than $\lambda 2200$. Well-marked effects were obtained with the lines between $\lambda 1849$ and $\lambda 2002$. On account of the much greater energy in the lines $\lambda 2257$ and $\lambda 2536$, the photo-electric effect for metals with these lines was many times greater than the effect with $\lambda 1849$. This shows clearly that the effect for anthracene must set in sharply somewhere between λ2002 and λ2200. There are no wave-lengths in the mercury-arc spectrum within this region to enable a closer approximation to be made.

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* Stark, *Phys. Zeit.* x. p. 614 (1909).

A linear relation between the maximum energy of emission and the frequency was found to represent the results for metals [*]. The law was expressed in the form

$$V = kn - V_0,$$

where V is the maximum velocity measured in volts (*i.e.* the potential difference required to bring the electron to rest), n the frequency, and k and V_0 are constants. The value of k—the gradient of the line connecting energy with frequency —does not vary much for metals, its mean value being about $3{\cdot}6 \times 10^{-15}$. Putting this into the equation and the ·87 volt corresponding to the wave-length λ1849, we get $V_0 = 5{\cdot}0$ volts. With these constants, k and V_0, we can calculate at what wave-length the emission velocity is zero, in other words, the wave-length at which the effect starts. The wave-length is λ2170, which is within the experimental limits λ2002 and λ2200. Hence we can say that the relation between the energy and the frequency is of the same order for anthracene as for metals.

The leaks corresponding to the wave-lengths λ1849 and λ2002 were much too small to enable me to determine the maximum emission velocities for the isolated wave-lengths, as this is a much more difficult experiment than determining whether a leak exists or not.

Oxides of Barium and Copper.

It may be interesting to place on record two experiments on oxides. (These surfaces were not prepared by distillation *in vacuo*.)

A disk of copper was made red-hot in air so as to cover the surface with a layer of oxide. It was then placed on the nickel disk N of fig. 1, and exposed to the light in the same way as the other compounds. Leaks of 4000 and 2600 were obtained from two different surfaces. These were far larger than the leaks from the salts, though they were of the order of 100 times less than the leak obtained from distilled metals under similar conditions.

In the second experiment, the nickel disk was covered with a thin layer of sealing-wax, and then strongly heated by the blowpipe until a white deposit was left. This is the process frequently adopted when making a "lime" cathode, though the deposit is, however, mainly barium oxide. The leak was never more than 4 units. The surface behaved like an imperfect insulator, for, after an exposure of several minutes, the leak was reduced to about half of its original value. On increasing the accelerating potential by a few volts, the leak increased to approximately its original value, showing that the diminution was not due to fatigue, but to the surface acquiring a positive charge, and thus reducing the effective accelerating potential almost to zero. It may be mentioned here that similar tests for poor conductivity in the other compounds were frequently tried. Their conductivity, however, appeared to be sufficient for these experiments.

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[*] Hughes, Phil. Trans. (A), vol. ccxii. p. 205 (1912).

Discussion of Results.

It was noticed, at the end of each experiment on the mercury salts, that the surface had a more or less grey metallic lustre. The appearance of the exposed part of the surface was quite different from that of the unexposed part. It is known that mercury salts are decomposed by ultra-violet light. In the case of the chlorides, there is no appreciable emission of electrons until after an exposure of thirty seconds or more. Then the effect increases with exposure, apparently showing that the effect of the light is to decompose the salt first of all, and then to act on the mercury surface as upon ordinary metals. This effect is more marked in the case of the iodides than in the case of the chlorides. This is readily explained by the fact that the iodides are more easily decomposed than the chlorides. It is difficult to say whether the small effect obtained in the first 20 seconds with the iodides is a real effect with the undecomposed salt. Analogy with the chlorides and other salts suggests that the decomposition sets in too rapidly for the initial stage, during which there is no emission, to be detected. The photo-electric behaviour of the antimony iodide appears to be an exception to the general rule.

In a paper recently published, Reboul[*] finds that the photo-electric leak from the halogen salts of copper and silver increases for a considerable time with exposure to light.

It is worthy of note that, in many cases, the leak decreases slightly after the salt has been kept in the dark, indicating perhaps that a partial recombination is taking place. Complete recombination is impossible as the charcoal absorbs any chlorine or iodine vapour which gets away from the surface.

It is not known whether lead iodide is decomposed by light. There was no trace of discoloration of the surface even after prolonged exposure. The leak, however, was much smaller than with the mercury salts. On the interpretation suggested above of an increasing photo-electric effect for salts, it appears that lead iodide is decomposed very slightly by light. It is possible that a photo-electric test of this kind may be a much more sensitive test for decomposition by light than any of the tests hitherto used.

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[*] Reboul, *Le Radium*, x. p. 155 (1912).

Putting aside the copper oxide, the magnitude of the photo-electric effect and the rapidity with which it sets in run more or less parallel with the heat of combination of the salt. Thus the most stable of the salts $ZnCl_2$ (when dry) shows no photo-electric effect at all, and the chlorides show, in general, a smaller effect than the iodides.

Several experiments show clearly that, if the distilled salt is not exposed to ultra-violet light for some hours, then only the small initial leak is obtained on the first exposure, proving that the increase in the effect depends upon exposure to light.

Summary.

1. An investigation has been made of the photo-electric effect in $ZnCl_2$, P_2O_5, PbI_3, HgI, HgI_2, $HgCl$, $HgCl_2$, $FeCl_3$, SbI_3, $BiCl_3$, the oxides of Ba and Cu, and anthracene.

2. Dry $ZnCl_2$ and P_2O_5 show no photo-electric effect. There is practically no effect for $FeCl_3$, and only a very small one for PbI_3 after exposure to ultra-violet light. The other halogen salts show well-marked effects after exposure to ultra-violet light.

3. The initial effect is either zero or very small for the halogen salts but, after exposure, increases in many cases to a large value. (SbI_3 is an exception to this rule.)

4. The explanation suggested is that the salts themselves are not photo-electric with wave-lengths longer than $\lambda 1849$, but that the light first of all decomposes the surface, and then acts on the metallic element in the ordinary way. The more stable the salt, the less is this effect.

5. The photo-electric effect in anthracene is produced entirely by wave-lengths shorter than $\lambda 2002$. The maximum emission velocity corresponding to $\lambda 1849$ is ·87 volt.

6. $ZnCl_2$ and P_2O_5 have no photo-electric effect when dry, but after contact with moist air they show a distinct effect. This effect cannot be accounted for by the photo-electric activity of water which, if it exists, is much too small.

I have pleasure in thanking Professor Sir J. J. Thomson for his interest and encouragement during this investigation.

The spectrograph used in some of these experiments was obtained by means of a Government Grant, through the Royal Society.

XXXIV. *Fundamental Properties of the Equation of State.*

By R. D. Kleeman, *D.Sc., B.A.*[*]

A General Form for the Equation of State.

THE equation of state of a substance must conform to the laws of thermodynamics. It should, therefore, be possible to deduce a fundamental form for the equation of state which takes these laws into account. Such a form for the equation can be easily obtained. It is shown in treatises on thermodynamics that $\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v$, where dQ denotes the amount of heat absorbed when the volume of the substance, whose mass will be taken as one gram, increases by dv at a constant temperature T, and dp denotes the change in pressure when the temperature changes by dT keeping the volume constant. Now $Q = \frac{1}{m_a}(U+u) + p\,.\,dv$ †, where U is the work done per molecule against the molecular attraction on separating the molecules by an infinite distance from one another, u is the internal energy of a molecule and m_a its absolute mass, and $p\,.\,dv$ the external work done when the volume of the substance changes by dv. Substituting this expression for Q in the thermodynamical equation and dividing it by T^2, and integrating we obtain

$$p = \frac{T}{m_a}\int\left(\frac{dU}{dv}\right)_T \frac{\delta T}{T^2} + \frac{T}{m_a}\int\left(\frac{du}{dv}\right)_T \frac{\delta T}{T^2} + \frac{T}{m_a}Z, \quad . \quad (1)$$

where Z is a function of v only. This is a fundamental form for the equation of state. It contains the three functions U, u, and Z, and its form is therefore completely obtained if the form of each of these functions is known. On consideration it will be evident that the state of a quantity of matter must be regulated by five things, viz., (1) the attraction of the molecules upon one another which gives rise to a negative potential energy represented per molecule by U, (2) the internal energy of a molecule represented by u, (3) the kinetic energy of a molecule, (4) the mass of a molecule, (5) the actual volume of a molecule. Since the equation of state must contain a function which represents the effect of the kinetic energy and actual volume of the molecules of a substance on its state, Z cannot be equal to zero. A molecule may have no actual volume in the strict sense of the term, for an atom may consist simply of a centre of force. In the present case its volume would be best defined as the volume of the space associated with it through which another molecule never passes. This volume probably depends on the temperature and other conditions of the substance.

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[*] Communicated by the Author.

† Proc. Camb. Phil. Soc. vol. xvi. pt. vi.

A number of properties of U and u can be deduced from equation (1) on comparing it with the facts. Let us suppose that $\left(\frac{d\mathrm{U}}{d\mathrm{T}}\right)_v=0$ and $\left(\frac{du}{d\mathrm{T}}\right)_v=0$, or that the force of attraction and the internal energy of a molecule in a substance at constant volume are independent of the temperature. This reduces equation (1) to $m_a p=-\left(\frac{d\mathrm{U}_1}{dv}\right)_\mathrm{T}-\left(\frac{du_1}{dv}\right)_\mathrm{T}+\mathrm{ZT}$. According to this equation the pressure of a substance at constant volume is a linear function of the temperature. But this does not agree with the facts. Hence one or both of the assumptions do not hold.

Next let us suppose that $\left(\frac{d\mathrm{U}}{d\mathrm{T}}\right)_v=0$ and $\left(\frac{du}{dv}\right)_\mathrm{T}=0$, or that the attraction of a molecule is independent of its temperature, and its internal energy independent of the vicinity of other molecules. These conditions reduce equation (1) to

$$p+\frac{1}{m_a}\left(\frac{d\mathrm{U}}{dv}\right)_\mathrm{T}=\frac{\mathrm{ZT}}{m_a}. \quad \text{Now } \frac{1}{m_a}\left(\frac{d\mathrm{U}}{dv}\right)_\mathrm{T}=\mathrm{P}_n$$

the intrinsic pressure of the substance*, and

$$p+\mathrm{P}_n=\frac{n}{2}2{\cdot}53\times10^{-20}\sqrt{\mathrm{T}m}\,\dagger,$$

where n denotes the number of molecules crossing per second a plane one cm.^{2} in area in one direction in the substance, and m is the molecular weight relative to hydrogen. Hence we obtain the simple equation

$$\mathrm{Z}=nm_a1{\cdot}26\times10^{-20}\sqrt{\left(\frac{m}{\mathrm{T}}\right)}$$

connecting Z and n. From the results obtained in previous papers ‡ it appears, however, that the above assumptions are not true, but approximately so.

Lastly, let us assume that $\left(\frac{d\mathrm{U}}{dv}\right)_\mathrm{T}=0$ and $\left(\frac{du}{dv}\right)_\mathrm{T}=0$, or that the molecules exert no attraction upon one another in the substance at the distance they are separated, and that the internal energy of a molecule is independent of the vicinity of other molecules. Equation (1) now becomes $p=ZT$. This formula is only realized in the case of a gas, showing that at the distance the molecules are then separated from one another these conditions are approximately fulfilled. When deviations from the formula occur, one or both of these conditions are not satisfied.

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* *Loc. cit.*

† Phil. Mag. July, 1912, pp. 101–118.

‡ *Loc. cit.*

Conditions satisfied by a Liquid and its Saturated Vapour.

In general the state of a substance is defined if the magnitude of two of the variables p, T, and v are known, except in the case of a liquid in contact with its saturated vapour, when it is necessary to know only the magnitude of one of the variables. Since in the latter case two variables take the place of one, namely, the volume of a gram of liquid and that of a gram of saturated vapour, there must exist another equation besides the equation of state by the help of which the variables can be determined if one of them is known. This is the well-known equation

$$\int_{v_1}^{v_2} p\,.\,\delta v = p(v_2 - v_1) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

obtained by means of the theory of continuity of state, and the thermodynamical principle that in an isothermal transformation the external work done is independent of the nature of the path described. The suffixes 1 and 2 refer to the liquid and its saturated vapour respectively.

The equations from which the variables T, p, v_1 and v_2 can be determined in terms of one of them are therefore

$$p = \frac{\mathrm{T}}{m_a}\int\left(\frac{d\mathrm{U}_1}{dv_1}\right)_{\mathrm{T}}\frac{\delta\mathrm{T}}{\mathrm{T}^2} + \frac{\mathrm{T}}{m_a}\int\left(\frac{du_1}{dv_1}\right)_{\mathrm{T}}\frac{\delta\mathrm{T}}{\mathrm{T}^2} + \frac{\mathrm{T}}{m_a}\mathrm{Z}_1, \quad . \quad (3)$$

$$p = \frac{\mathrm{T}}{m_a}\int\left(\frac{d\mathrm{U}_2}{dv_2}\right)_{\mathrm{T}}\frac{\delta\mathrm{T}}{\mathrm{T}^2} + \frac{\mathrm{T}}{m_a}\int\left(\frac{du_2}{dv_2}\right)_{\mathrm{T}}\frac{\delta\mathrm{T}}{\mathrm{T}^2} + \frac{\mathrm{T}}{m_a}\mathrm{Z}_2, \quad . \quad (4)$$

$$(v_2 - v_1)p = \frac{\mathrm{T}}{m_a}\int\left(\frac{\mathrm{U}_2 - \mathrm{U}_1}{\mathrm{T}^2}\right)\delta\mathrm{T} + \frac{\mathrm{T}}{m_a}\int\left(\frac{u_2 - u_1}{\mathrm{T}^2}\right)\delta\mathrm{T} + \frac{\mathrm{T}}{m_a}\int_{v_1}^{v_2}\mathrm{Z}\,.\,\delta v. \quad . \quad . \quad . \quad . \quad (5)$$

Therefore if the form of each of the functions U, u, and Z were known, the equations could be completely set down. It will be recognized that U_1 is the work done per molecule against the molecular attraction on separating the molecules of the liquid by an infinite distance from one another, and u_1 is the internal energy of a molecule in the liquid, and U_2 and u_2 are the corresponding quantities for the saturated vapour.

Another equation connecting p, T, v_1 and v_2 can be obtained from Clapeyron's equation. Since L the internal heat of evaporation is equal to $\frac{1}{m_a}(U_1-U_2+u_1-u_2)$ the equation may be written

$$U_1-U_2+u_1-u_2=m_a(v_2-v_1)T\frac{dp}{dT}. \quad . \quad . \quad . \quad (6)$$

If p, v_1 and v_2 be expressed in terms of T from equations (3), (4), and (5), and substituted in equation (6) it should identically vanish.

Conditions to be satisfied by the Equation of State at the Critical Point.

The equation of state must satisfy a number of conditions at the critical point. The conditions usually given are

$$\int=0, \quad \frac{df}{dv}=0, \quad \frac{d^2f}{dv^2}=0, \quad . \quad . \quad . \quad . \quad (7)$$

where the first equation denotes the equation of state. These conditions have been obtained from considerations of the continuity of state. But a number of others can be found which the equation of state must satisfy.

One of them is equation (6) which becomes

$$\frac{U_1-U_2}{v_2-v_1}+\frac{u_1-u_2}{v_2-v_1}=\frac{dU}{dv}+\frac{du}{dv}=m_a\left(T\frac{dp}{dT}-p\right) \quad . \quad (8)$$

at the critical point.

Another equation is obtained as follows. Let us write $L_1=A_1v_1$ and $L_2=A_1v_2x$, where L_1 is the energy necessary to separate the molecules of a gram of liquid by an infinite distance from one another, L_2 the corresponding energy necessary for a gram of the saturated vapour, and A_1 and x are appropriate functions of T. We have then $L=L_1-L_2$, and Clapeyron's equation becomes

$$A_1(v_1-v_2x)=(v_2-v_1)\left(T\frac{dp}{dT}-p\right).$$

At the critical point $x=1$, and the equation becomes

$$A_1=p-T\frac{dp}{dT}. \quad \text{Now } L_1=\frac{1}{m_a}(U_1+u_1-u_a),$$

where u_a is the value of u when $v=\infty$, the corresponding value of U being equal to zero. Hence at the critical point

$$U+u-u_a=m_a v\left(p-T\frac{dp}{dT}\right). \quad . \quad . \quad . \quad . \quad (9)$$

The value of the expression $\left(p-T\frac{dp}{dT}\right)$ at the critical point can be easily obtained from the facts. It is found to be equal to $6{\cdot}5\,p_c$*. A knowledge of the value of this expression increases the value of equations (8) and (9) considerably.

The equations of condition at the critical point written out more fully are thus

$$\frac{m_a p}{T}=\int\left(\frac{dU}{dv}\right)_T\frac{\delta T}{T^2}+\int\left(\frac{du}{dv}\right)_T\frac{\delta T}{T^2}+Z, \quad . \quad . \quad (10)$$

$$0=\int\left(\frac{d^2U}{dv^2}\right)_T\frac{\delta T}{T^2}+\int\left(\frac{d^2u}{dv^2}\right)_T\frac{\delta T}{T^2}+\frac{dZ}{dv}, \quad . \quad (11)$$

$$0=\int\left(\frac{d^3U}{dv^3}\right)_T\frac{\delta T}{T^2}+\int\left(\frac{d^3u}{dv^3}\right)_T\frac{\delta T}{T^2}+\frac{d^2Z}{dv^2}, \quad . \quad (12)$$

$$6{\cdot}5\,m_a p=-\frac{dU}{dv}-\frac{du}{dv}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and $$6{\cdot}5\,m_a v p= U+u-u_a. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Possibly other conditions exist besides those given.

A remark should be made here in connexion with the use to which equations (7) have been put. The equation of state is often written in the form $p+P_n=H$, where P_n is the intrinsic pressure and H a function of T and v expressing the effect of the motion of translation of the molecules. Attempts have been made to obtain the form of P_n and H by substituting for each an expression containing a number of undetermined constants, and then to determine these constants by means of equations (7). But this is not mathematically sound, and may therefore lead to quite erroneous results. It is evident that if we substitute for P_n and H in the equation the expressions $(P_n+\phi(v, T))$ and $(H+\phi(v, T))$ respectively, it reduces to its original form. It follows therefore that the exact forms of P_n and H consist of the expressions obtained in the above way plus an undetermined function $\phi(v, T)$.

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* Phil. Mag. Oct. 1911, p. 584.

Conditions to be satisfied at the Absolute Zero by the Equation of State.

One of these conditions is $$p=0, \quad . \quad . \quad . \quad . \quad (15)$$

when $v=v_1$ and $v=v_2=\infty$.

Two more conditions are obtained on applying equations (2) and (6) to the substance. The equations can then be simplified. Since $p=0$ and v_1 is finite, $pv_1=0$. The saturated vapour then behaves as a perfect gas, and consequently $pv_2=\frac{\mathrm{RT}}{m}=0$. It follows therefore that $p(v_2-v)=0$. In a subsequent paper it will be shown that $\frac{dp}{d\mathrm{T}}=0$. The equations then become

$$\mathrm{U}_1+u_1-u_a=\frac{\mathrm{RT}^2}{p}\frac{dp}{d\mathrm{T}}, \quad . \quad . \quad . \quad . \quad (16)$$

$$\int_{v_1}^{v_2} p \,.\, dv=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

We must also have $$\left(\frac{dp}{dv}\right)_{\mathrm{T}}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

when $v=v_2=\infty$. This follows at once from a consideration of the isothermals of the substance. If the volume of the substance keeping its temperature at the absolute zero is gradually increased the pressure will decrease, since the substance increasingly behaves as a perfect gas. The p axis is therefore asymptotic to the isothermal for $\mathrm{T}=0$, and hence when $v=\infty$ the above equation must hold.

It should be pointed out that the foregoing conditions are not included in the conditions applying to the critical point. Thus suppose that the constants in the equation of state are determined by means of all these conditions. Let us assume, for example, that the equation of state contains expressions of the form $(\mathrm{A}+\mathrm{TB})$. In the first of equations (7) this expression becomes $(\mathrm{A}+\mathrm{T}_c\mathrm{B})$, and in equation (15) it becomes A. Thus the equations obtained would not be the same.

The Law of Corresponding States.

This law has been deduced by van der Waals from his equation of state. It does not seem to be generally recognized, however, that the deduction rests on very weighty tacit assumptions. It is necessary therefore to investigate it a little more closely.

The constants in the equation of state will obviously depend on the units of pressure, volume, and temperature chosen. The fundamental form of the equation is therefore that which is independent of the nature of the units. This form is

$$\phi\left(\frac{\mathrm{T}}{\mathrm{T}_c}, \frac{v}{v_c}, \frac{p}{p_c}\right)=0, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

that is an equation which contains only the ratios $\frac{\mathrm{T}}{\mathrm{T}_c}$, $\frac{v}{v_c}$, and $\frac{p}{p_c}$, where p_c, v_c, T_c denote the critical values of p, v, and T. Now if we assume that the algebraical form of this equation is the same for all pure substances, the law of corresponding states at once follows. Thus in the case of a substance whose state is defined by two variables, it follows directly from the above equation. When the state of a substance is defined by one variable it follows from equations (3), (4), and (5), each of which reduces to the same form as the above equation.

Or we may deduce the law thus. Let us assume, (1) that the algebraical form of the equation for each pure substance is the same, except that some of the constants it contains depend on the nature of the substance, (2) that the conditions it has to satisfy at the critical point and absolute zero are the same for each substance, and are sufficient in number to determine the nature of the foregoing constants. The general equation of state is then of the form $\psi(\mathrm{T}, v, p, \mathrm{T}_c, v_c, p_c)=0$. Now this equation must be independent of the kind of units adopted, and therefore reduce to the same form as equation (19).

We thus see that in obtaining the law of corresponding states from the equation of state some very weighty assumptions are made which amount almost to assuming the law without making any further deductions. There is nothing from which we can argue that these assumptions must hold. It appears that they do not hold for substances partly polymerized, since these do not obey the law of corresponding states. But there is no obvious reason why this should be so. At the end of the next section we will show that the law can be made to depend on more fundamental assumptions than those just considered.

The General Forms of U, u, *and* Z.

The law of corresponding states enables us to obtain some information about the general forms of U, u, and Z. Let us assume that $\mathrm{U}=\mathrm{X}+\mathrm{W}$, $u=x+w$, and $\mathrm{Z}=\mathrm{Y}+z$, where W and w may be functions of any form of T and v, z any function of v, and X, x, and Y such functions as will reduce each of the equations (3), (4), (5), and (6) to the same form as equation (19) if substituted for U, u, and Z, respectively. Now in order that these equations should reduce to the same form when the values of U, u, and Z given by the above equations are substituted, we must have

$$\int\left(\frac{dW_1}{dv_1}\right)_T\frac{\delta T}{T^2}+\int\left(\frac{dw_1}{dv_1}\right)_T\frac{\delta T}{T^2}+z_1 \qquad =0, \quad (20)$$

$$\int\left(\frac{dW_2}{dv_2}\right)_T\frac{\delta T}{T^2}+\int\left(\frac{dw_2}{dv_2}\right)_T\frac{\delta T}{T^2}+z_2 \qquad =0, \quad (21)$$

$$\int\frac{W_1-W_2}{T^2}\delta T+\int\frac{w_1-w_2}{T^2}\delta T+\int_{v_1}^{v_2}z\,.\,\delta v=0, \quad (22)$$

and $$W_1-W_2+w_1-w_2 \qquad =0. \quad (23)$$

Subtracting equation (21) from equation (20) and substituting for (W_1-W_2) from equation (23), we obtain $z_1=z_2$. Now this can only be in general the case if z is independent of v, that is a constant, which may of course be equal to zero. The same result can be deduced from equations (23) and (22). Equation (23) may be written $W_1+w_1=W_2+w_2$. It will now be seen that this equation can hold in general only if the quantities in the equation are independent of v, and thus functions of T only. It follows then that $W_1=W_2$ and $w_1=w_2$. Now W_1 or W_2 is equal to zero. For U or X+W is by definition the work done per molecule against molecular attraction on separating the molecules an infinite distance from one another when their initial volume is v. Now this work could not contain a term that is a constant or depends on the temperature only, and thus is independent of the initial and final volume of the substance. W_1 and W_2 are therefore in general each equal to zero, and w_1 and w_2 each a function of the temperature which we will denote by $\psi(T)$. From equations (20) and (21) it follows now that $z_1=0$, and $z_2=0$, or $z=0$ in general. We have then U=X, $u=x+w$, and Z=Y. Since equation (1) must reduce to the same form as equation (19) when we put U=X, $u=x$, and Z=Y, it follows that

$$U=X=\frac{m_a p_c}{T_c}\cdot\phi_1\left(\frac{T}{T_c},\frac{v}{v_c}\right),\ u=x+w=\frac{m_a p_c}{T_c}\cdot\phi_2\left(\frac{T}{T_c},\frac{v}{v_c}\right)+\psi(T),$$

and $$Z=\frac{m_a p_c}{T_c}\cdot\phi_3\left(\frac{v}{v_c}\right).$$

It should be noticed that not only need w not be a function conforming to the law of corresponding states, but its form need not be the same for each substance. In a subsequent paper I will show that w is not zero (as it might be), but a function of T whose form depends on the nature of the substance.

It will be easily seen that the law of corresponding states can be deduced if we assume that the functions U, u, and Z have the forms given by the above equations.

Special Forms of the Equation of State.

The equation of state is often written, as we have already remarked, in the form $p+P_n=\phi(T, v)$, where P_n denotes the intrinsic and p the external pressure, and $\phi(T, v)$ the effect of the motion of translation of the molecules which balances the intrinsic and external pressure. Van der Waals writes $\frac{RT}{m(v-b)}$ for the right-hand side of the equation, where b is equal to four times the volume actually occupied by the molecules of a gram of matter. The equation would then strictly hold if the average velocity of a molecule and its chance of colliding with another molecule is not affected by the attraction of the molecules upon one another. But this is by no means the case, as I have shown in a previous paper[*]. It was shown that when a molecule passes through a point in a substance at which the forces of attraction of the surrounding molecules neutralize one another, its velocity is equal to that it has in the gaseous state at the same temperature. But the average velocity increases with the density of the substance when it does not obey the laws of a perfect gas, and in the case of a liquid is from five to ten times the foregoing velocity. Further evidence of this will be brought forward in a subsequent paper.

It is necessary therefore to change van der Waals' expression into a form taking this fact into account. The pressure exerted by the molecules per cm.^{2} in a substance (balancing the intrinsic and external pressure) is proportional to the number of molecules crossing a cm.^{2} per sec. in one direction[†]. This number is proportional to the average velocity other things remaining the same. It is evident then that we must multiply the expression by $\frac{V_a}{V}$, where V_a is the average velocity of a molecule and V its velocity in the gaseous state at the same temperature.

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[*] *Loc. cit.*

[†] *Loc. cit.*

But even then the expression will represent only approximately the facts. The value of b cannot be constant since the chance of one molecule *actually* colliding with another must be affected by their attraction upon one another. Thus let σ_1 denote the radius of the sphere of action of each molecule which gives rise to actual collisions between them, and σ_2 the actual radius of each molecule. The ratio of the chance of an actual collision occurring when the molecular attraction is acting to that when it is supposed not to be acting is $\frac{\sigma_1^2}{\sigma_2^2}$. We must therefore write for b the expression $\frac{\sigma_1^2}{\sigma_2^2} \times \frac{16}{3}\pi\sigma_2^3 = \frac{16}{3}\pi\sigma_1^2\sigma_2$ instead of $4 \times \frac{4}{3}\pi\sigma_2^3$. The modified equation of state is then

$$p + P_n = \frac{V_a}{V} \frac{RT}{m\left(v - \frac{16}{3}\pi\sigma_1^2\sigma_2\right)} = \left(\frac{RT}{3m}\right)^{1/2} \frac{V_a}{\left(v - \frac{16}{3}\pi\sigma_1^2\sigma_2\right)}, \quad \ldots \quad (24)$$

since $V = \left(\frac{3RT}{m}\right)^{1/2}$ according to the kinetic theory of gases.

The value of σ_1 must depend on the density of the substance when the molecules are under each other's influence, since the effect of the attraction of a molecule upon another is then modified by the surrounding molecules. Thus, for example, a molecule passing midway between two molecules at right angles to the line joining their centres, is not affected by either of them. It is evident from this example that σ_1 decreases with increase of density of the substance. This explains why the value of b in van der Waals' equation is approximately constant, for as σ_1 decreases V_a increases, the joint effect of which could conceivably be represented by van der Waals' expression. It is obvious that b and $\frac{16}{3}\pi\sigma_1^2\sigma_2$ must be of the same order of magnitude.

The fact that van der Waals' equation gives values of b from which the radius of a molecule can be determined which agrees well with that obtained by other methods, is not conclusive evidence of the correctness of the assumptions made. One reason is stated above. Another is that when an equation contains more constants than one, their values can usually be varied over a considerable range without seriously affecting the agreement of the equation as a whole with the facts. The values of constants determined by simultaneous equations are therefore of less value than those determined directly.

An expression for σ_1 in terms of the density of the substance will be obtained in a subsequent paper[*]. We shall then also obtain some information about the form of the expression for V_a, using the critical point conditions given in this paper. These conditions will also be used to determine the approximate form of the arbitrary function in the law of molecular attraction given by the writer[†].

London, April 10, 1912.

XXXV. *On the Secondary Rays excited by the α Rays of Polonium.*—II. *By* V. E. Pound, *M.A.*[‡]

1. *Introduction.*

IN a previous paper by the writer[§] it has been shown that when the α rays of polonium strike a carbon or a brass plate secondary rays are produced which are similar to the δ rays of polonium. It has been shown, too, that a very considerable part of this secondary radiation is due to the presence of gas occluded at or deposited on the surface of the brass or carbon plate. The present paper describes some further experiments on the influence of this gaseous layer on the secondary radiation excited in different substances when these are subjected to bombardment by the α rays of polonium.

2. *Description of Apparatus.*

The apparatus used for the investigation was composed of a brass tube A about 3 cm. in diameter and 18 cm. long, one end of which was closed air-tight by an ebonite plug sealed in with wax. Centrally through this plug was led a brass rod, B, carrying a brass plate, C, upon which a thin circular piece of polonium-coated brass about 1·5 cm. in diameter was fixed. A brass ring, D, passed through the ebonite and connected to earth served as a guard ring. At the other end of the tube A a smaller tube E, 1·5 cm. in diameter, was inserted and soldered in position at the top so as to be co-axial with the former. In this way the space between the tubes A and E was made air-tight. The lower end of the tube E was closed by means of a thin brass sheet, and a flat circular plate, K, of carbon or metal was held against this thin brass sheet by means of a flanged collar F provided with a screw. The distance between the polonium and the lower face of the carbon or brass plate was ·6 cm. The whole apparatus was connected by a tube G to a Gaede pump and a McLeod gauge. The apparatus was insulated by mica and supported in such a way that the polonium and the circular plate opposite the polonium were symmetrically placed between the poles of a powerful electromagnet. The circular plate held at F could be altered in temperature by liquid air or some other liquid of constant temperature in the tube E. The polonium was connected by means of the brass rod B and a screened connecting wire to an electrometer of moderate sensibility.

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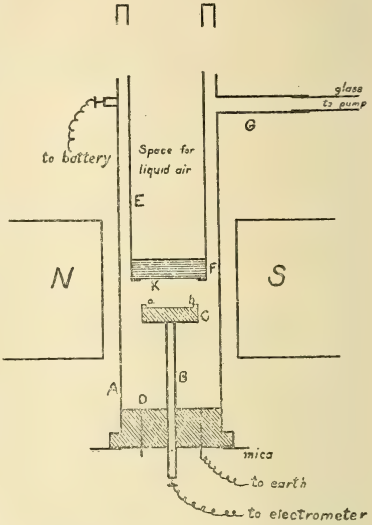
[*] Proc. Camb. Phil. Soc. vol. xvi. pt. vii.

[†] Ibid. pt. viii.

[‡] Communicated by Professor J. C. McLennan. Read before the Canadian Institute, Toronto, January 13, 1912.

[§] Trans. Canadian Institute, 1912; Phil. Mag. May 1912.

Fig. 1.



3. *Experiments with Carbon at Different Temperatures.*

The method of conducting the experiments was as follows. The carbon plate K was charged to a negative potential of about 80 volts by connecting the outer part of the apparatus to a battery. This high negative potential on the carbon was sufficient to prevent any δ rays from leaving the polonium. The Gaede pump was set exhausting the gas from the apparatus, and seven minutes after the pump was started the pressure of the gas was read by a McLeod gauge, and the rate of charging of the polonium was measured by the electrometer. The charge which came to the polonium was negative, and consisted of a current of α rays leaving the polonium, a current of secondary rays coming from the carbon to the polonium excited by the α ray bombardment on the carbon, and an ionization current through the remaining gas in the chamber. Readings of the charge which accrued on the polonium plate were made at definite intervals of time afterwards until the rate of charging of the plate became fairly constant. This constant value, as shown in the previous paper*, was reached when the density of the layer of gas occluded in the surface of the carbon was in equilibrium with the pressure of gas in the vessel, that is, when there was no readjustment going on in the gaseous layer. After the rate of charging of the polonium had become fairly constant a weak magnetic field was established by passing a small current through the electromagnet, and the rate of charging of the polonium was again found. Then larger and larger currents were sent through the electromagnet, and readings were taken until the rate of charging of the polonium became constant. This last constant charge which came to the polonium was composed of the α ray current leaving the polonium and the ionization current through the gas. The magnetic field was used to deflect the slow-moving secondary rays coming from the carbon, and the constant rate of charging of the polonium denoted that the magnetic field had deflected them all. The influence of the magnetic field in deflecting the α rays or the ionization current through the gas was probably very small. Accordingly the difference between the first constant value of the rate of charging of the polonium and the last constant value was a measure of the magnitude of the secondary ray current from the carbon excited by the α ray bombardment.

In the following tables the results obtained with air-filled carbon, first at a temperature of 110° C., second at room temperature, third at a temperature given by a mixture of solid carbonic acid gas and ether, namely $-78°$ C., and, lastly, at liquid-air temperature $-192°$ C., are given. After each experiment air was allowed to remain in the apparatus at atmospheric pressure until the next experiment. Before beginning the set of experiments a piece of carbon, the surface of which was freshly cut and which had never before been exposed to α rays, was placed in the apparatus. For comparison all the readings were reduced to the same date by the use of the standard equation

$$I = I_0 e^{-\lambda t};$$

the half decay period of the polonium being taken as 140 days†.

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* Trans. Canadian Institute, 1912; Phil. Mag. May 1912.

† See 'Physical and Chemical Constants,' by Kaye and Laby, p. 107.

Table I.—Air in Apparatus.
Carbon electrode at temperature 110° C.
Charge on carbon = −83 volts.

Pressure of air in vessel.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·02	0	0	−203
·007	5	0	−185
·007	15	0	−173
·004	30	0	−169
·003	45	0	−162
·006	60	0	−166
·003	68	0	−162·5
·005	90	0	−162
·004	...	1	−98
·002	...	6	−41
·002	...	15	−39·2
·002	...	23·5	−37·8

Table II.—Air in Apparatus.
Carbon electrode at temperature 23° C.
Charge on carbon = −83 volts.

Pressure of air in vessel.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·02	0	0	−254
·006	5	0	−209·5
·003	15	0	−180
·003	33	0	−165
·002	45	0	−158
·002	60	0	−158
·002	...	1	−57·8
·002	...	5·5	−38
·002	...	12	−37·4
·002	...	18·5	−37·4
·002	...	26	−37·4

Table III.—Air in Apparatus.
Carbon electrode at temperature −78° C.
Charge on carbon = −84 volts.

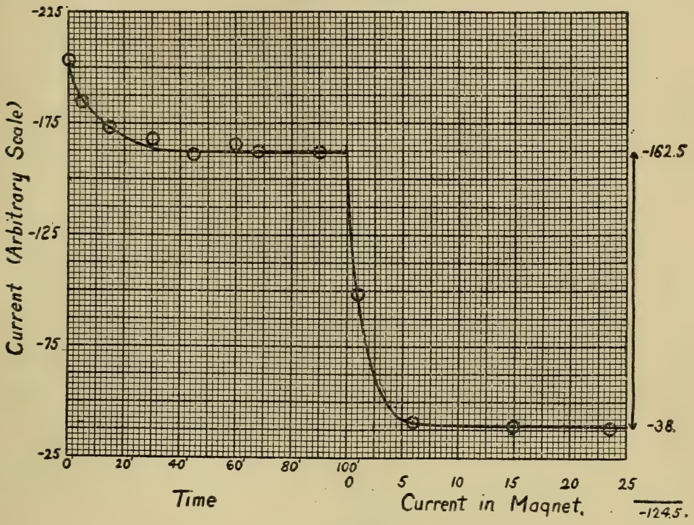
Pressure of air in vessel.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·02	0	0	−161·5
·004	5	0	−157·7
·003	15	0	−159·2
·001	30	0	−161·5
·001	45	0	−165
·001	70	0	−172
·001	90	0	−176
<·001	105	0	−178
<·001	140	0	−182
<·001	155	0	−184
<·001	...	1	−36·5
<·001	...	6	−35
<·001	...	11	−35
<·001	...	17·5	−33
<·001	...	24	−35

Table IV.—Air in Apparatus.
Carbon electrode at temperature −192° C.
Charge on carbon = −84 volts.

Pressure of air in vessel.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·03	0	0	−269
·009	5	0	−245
·004	15	0	−246
·004	25	0	−245
·002	40	0	−249
·002	55	0	−252
·002	70	0	−253·8
·001	85	0	−256
·001	100	0	−262
·001	118	0	−262
·001	...	1	−37
001	...	5·5	−35
·001	...	11	−34
·001	...	16·5	−34
·001	...	24·5	−34·4

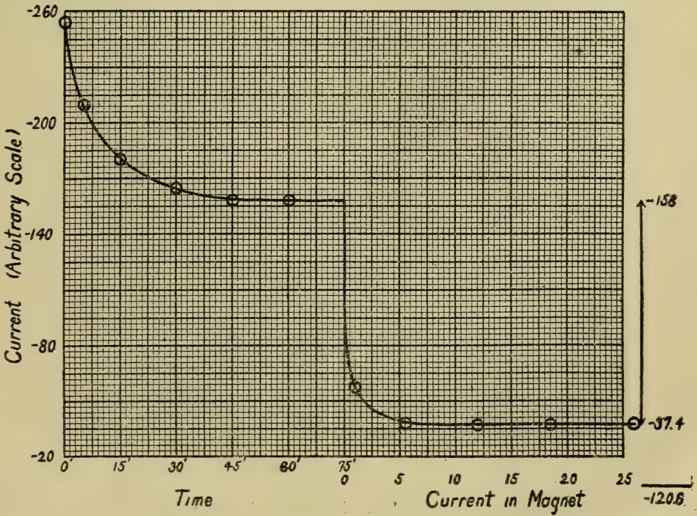
The results given in these tables are plotted in figs. 2, 3, 4, and 5. The curve drawn on the first half of each figure shows the way the rate of charging of the polonium decreased or increased with the time until it became approximately

Fig. 2.



110°C Air.

Fig. 3.



23° C Air

Fig. 4.

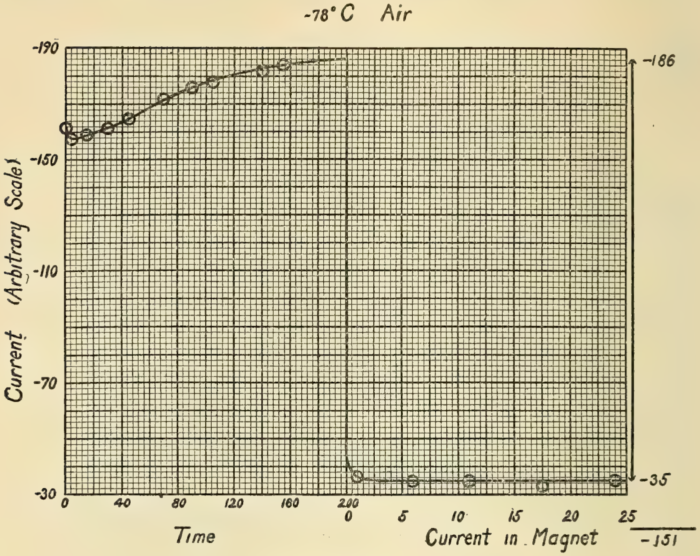
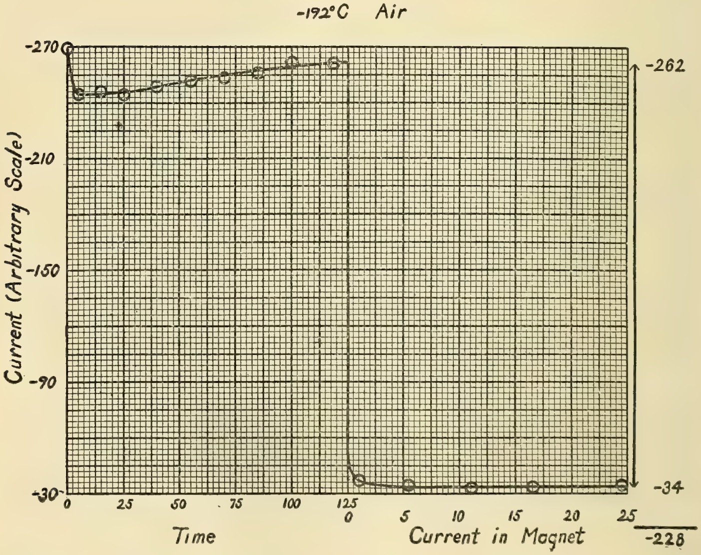


Fig. 5.



constant. The curve drawn on the remaining half of the figure shows the way the rate of charging of the polonium decreased to a constant value as the magnetic field was gradually increased from zero upwards. The curves drawn on the first half of fig. 4 and of fig. 5 show a remarkable difference from the corresponding curves in figs. 2 and 3. The curves of figs. 2 and 3 drop gradually with the time and come to a constant value, while the curves of figs. 4 and 5 first decrease and then increase to an approximately constant value. The only difference in the conditions under which the experiments were made was a difference in the temperature of the carbon. When the carbon was at room temperature or at a temperature of 110° C. the rate of charging of the polonium decreased with the time before becoming constant, while when the carbon was at −78° C. or at −192° C. the rate of charging decreased slightly and then increased. The cause of this difference is readily seen when it is remembered that carbon occludes more air at a low temperature than at a high, and that the α rays excite secondary rays in the air layer on the surface of the carbon as well as in the carbon itself *. When the temperature of the carbon is high the air readily comes away from the surface of the carbon, and hence the secondary radiation decreases. When the temperature of the carbon is low the air does not come away, but becomes denser and denser at the surface of the carbon as it oozes out of the interior, and also as it comes out of the cooled brass walls of the apparatus. (It will be shown later that air is expelled from brass as it is cooled.) Therefore, instead of a decrease there is set up a gradual increase in the secondary radiation as the air layer becomes denser.

The final value of the secondary radiation from the carbon and the air layer at its surface was obtained in each case by taking the difference between the constant rates of charging of the polonium without and with the applied magnetic field. In the following table the values of the secondary radiation with the carbon at the several different temperatures are set down.

TABLE V.

Fresh Carbon in Air.
Secondary Radiation from Carbon and Air Layer.

Temperature of Carbon...	110° C.	23° C.	−78° C.	−192° C.
Secondary Radiation......	−124·5	−120·6	−151	−228

It will be seen from the table that when the carbon was

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* Pound, Trans. Canadian Institute, 1912; Phil. Mag. May 1912.

at the temperature of 23° C. the secondary radiation excited by the α rays was $-120{\cdot}6$, and when the carbon was at 110° C. the secondary radiation was $-124{\cdot}5$. These numbers are very nearly the same, and accounting for their difference by experimental error, they show that the amount of α ray excited secondary radiation from carbon was the same when the carbon was at 23° C. as when it was at 110° C. Since this secondary radiation most probably comes from both the carbon and its air layer, the coincident values of the secondary radiation from carbon at the two temperatures would indicate that the density of the gaseous layer at the surface of the carbon was the same at the two temperatures. When the carbon was at $-78°$ C., however, the secondary radiation from it amounted to -151, *i. e.* an increase of about 24 per cent. over the value of the secondary radiation when the carbon was at room temperature. Again, when the carbon was at $-192°$ C. the secondary radiation was -228, or an increase of 87 per cent. above the value at room temperature. These large increases in the secondary radiation when the carbon was at the lower temperatures is readily accounted for by the increase in the secondary radiation from the gaseous air layer at the surface of the carbon, which increases in density as the temperature is lowered.

In order to find out whether this same effect would occur when the carbon was in other gases than air experiments were also tried with oxygen and hydrogen. A fresh piece of carbon was used for each gas. The air which was occluded in the fresh piece of carbon on account of its being in an atmosphere of air was got rid of by putting the carbon in the apparatus, and exhausting and leaving it for a long time. The apparatus was then filled with the gas which was to be experimented upon, and left for some time in order that the carbon might take up the new gas as much as possible. After this the carbon was cooled or heated to the desired temperature, the gas was pumped from the apparatus, and a series of readings was taken, in the manner indicated above, of the rate of charging of the polonium, both with and without the magnetic field. The same characteristic results were obtained with these gases at the different temperatures as with the air. The readings taken with the carbon at temperatures 115° C., 23° C., $-78°$ C., and $-192°$ C., in an atmosphere of oxygen are given in Tables VI., VII., VIII., and IX. below, and the readings taken with the carbon at temperatures 24° C. and $-192°$ C. in an atmosphere of hydrogen are given in Tables X. and XI.

TABLE VI.

Oxygen in Apparatus.
Carbon electrode at temp. 115° C.
Charge on carbon = −84 volts.

Pressure of air in vessel.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·05	0	0	−219·5
·012	5	0	−199·5
·008	15	0	−189·5
·005	25	0	−182
·003	102	0	−157
·001	114	0	−157
< ·001	130	0	−158
< ·001	133	0	−158
< ·001	...	1	− 42
< ·001	...	9	− 34·5
< ·001	...	15	− 32·8
< ·001	...	23·5	− 32·8

TABLE VII.

Oxygen in Apparatus.
Carbon electrode at temp. 23° C.
Charge on carbon = −84 volts.

Pressure of air in vessel.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·06	0	0	−184
·015	5	0	−175
·006	15	0	−159
·003	30	0	−156
·003	40	0	−156
·001	55	0	−155
·001	70	0	−155
·001	86	0	−155
·001	...	1	− 38
·001	...	5·5	− 34
·001	...	12	− 34
·001	...	20	− 32
·001	...	25	− 34

TABLE VIII.

Oxygen in Apparatus.
Carbon electrode at temp. − 78° C.
Charge on carbon = − 83 volts.

Pressure of air in apparatus.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·045	0	0	−206·5
·011	5	0	−190
·005	15	0	−187
·003	30	0	−185·5
·003	45	0	−188
·003	60	0	−187
·002	75	0	−188
·002	90	0	−190
·002	128	0	−193·5
·002	132	0	−193·5
·002	...	1	− 36·2
·002	...	12	− 34·2
·002	...	18	− 34·2
·002	...	25	− 33·4

TABLE IX.

Oxygen in Apparatus.
Carbon electrode at temp. −192° C.
Charge on carbon = − 84 volts.

Pressure of air in apparatus.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·08	0	0	−277
·012	5	0	−237
·006	15	0	−224·5
·004	30	0	−224·5
·004	45	0	−229
·003	60	0	−224·5
·003	75	0	−227·5
·003	90	0	−225
·003	...	1	− 35·5
·003	...	5	− 33·4
·002	...	13	− 32·6
·003	...	19	− 33·4
·002	...	24·5	− 33·4

TABLE X.

Hydrogen in Apparatus.

Carbon electrode at
temperature 24° C.
Voltage on carbon
= −84 volts.

Pressure of air in apparatus.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·006	0	0	−429·5
·002	10	0	−230·5
·001	20	0	−205
<·001	40	0	−202
<·001	60	0	−196
<·001	90	0	−194
<·001	...	1·5	− 66
<·001	...	4·5	− 47·5
<·001	...	9	− 48·5
<·001	...	18	− 49
<·001	...	24·5	− 47

TABLE XI.

Hydrogen in Apparatus.

Carbon electrode at
temperature −192° C.
Voltage on carbon
= − 84 volts.

Pressure of air in apparatus.	Time from initial reading taken 7 min. after starting pump.	Current through magnet.	Current to polonium.
mm.	min.	amp.	
·015	0	0	−256
·004	5	0	−212
·002	22	0	−213
·001	29	0	−227·5
·001	39	0	−238
<·001	52	0	−242
<·001	65	0	−254
<·001	80	0	−249
<·001	95	0	−266
<·001	115	0	−272
<·001	130	0	−273
<·001	...	1·5	− 39·6
<·001	...	4	− 37·5
<·001	...	9·5	− 36·8
<·001	...	15·5	− 36·8
<·001	...	25	− 36·2

From these results the values of the secondary radiation from the carbon at different temperatures in oxygen and in hydrogen were deduced as with the air, by taking the difference between the final rates of charging of the polonium without and with the magnetic field applied. These are given in Tables XII. and XIII.

TABLE XII.

Fresh Carbon in Oxygen.
Secondary Radiation from Carbon and Oxygen Layer.

Temperature of Carbon...	115°	23°	−78°	−192°
Secondary Radiation......	−124·7	−121·5	−160	−193

TABLE XIII.

Fresh Carbon in Hydrogen.

Secondary Radiation from Carbon and Hydrogen Layer.

Temperature of Carbon	24° C.	−192° C.
Secondary Radiation................	−147	−233

Here, again, we find that both with oxygen and with hydrogen the results show that the secondary radiation was much greater when the carbon was at a low temperature than when it was maintained at a higher temperature.

From the foregoing it is clear that this modification of the intensity of the secondary radiation is attributable, as in the case of air, to an increase in the amount of gaseous oxygen and hydrogen occluded in the surface of the carbon by a reduction of the temperature.

From the experiments just described it follows that the amount of secondary radiation obtained from an electrode under bombardment by α rays may be taken as a measure of the density of the gaseous layer at the surface of the electrode when the latter is placed in a gas at a very low pressure. If there were no difference in the secondary radiation from a substance at different temperatures under the conditions mentioned it would indicate either that there was no gaseous layer at the surface of the substance bombarded, or else that the density of the gaseous layer adhering to it was the same at all temperatures. In the following section an experiment is described which makes use of this conclusion.

4. *Experiments with Brass.*

A peculiar effect was observed during the course of all the experiments, namely, that it took a longer time to reduce the pressure of the gas in the apparatus to a low value when the walls of the vessel were cooled with liquid air, than when the walls were at ordinary room temperature. At first this effect was supposed to be due to some leak in the apparatus, and the vessel was removed and carefully tested under pressure for small holes or porous places in the brass. But invariably it was found that no such holes or porous places could be discovered. It was also found that when the apparatus was put back and exhausted at ordinary temperatures the pressure was reduced with the same speed as before the apparatus was cooled with liquid air. There seemed, therefore, to be no leak of air through the walls of the apparatus, and the only other explanation that could be offered was that a gas came from the walls of the brass vessel at liquid air temperature which did not come at room temperature. If this were the case there would be less gas in the brass at low temperature than at high, and the method indicated in the previous section of studying the gaseous layer at the surface of a substance by the quantity of secondary rays coming from it could be used to test the above explanation. Accordingly, a brass plate was placed at K instead of a carbon one, and the amount of α ray excited secondary radiation from the brass plate was determined when it was at room temperature and when it was at the temperature of liquid air. The series of readings taken are given in Tables XIV. and XV. In order that the brass when at room temperature might be as free from air as possible the pump was made to exhaust the air from the apparatus for three hours continuously before a reading was taken of the rate of charging of the polonium.

TABLE XIV.

Air in Apparatus.

Brass Electrode at 20° C. Voltage on Brass = −81 volts.

Pressure of air in apparatus.	Time from initial reading 3 hours after starting pump.	Current through magnet.	Current to polonium.
< ·001 mm.	0 min.	0 amp.	−238·5
< ·001 ,,	5 ,,	0 ,,	−237
< ·001 ,,	15 ,,	0 ,,	−238·5
< ·001 ,,	...	1 ,,	− 40·5
< ·001 ,,	...	10 ,,	− 34·5
< ·001 ,,	...	17 ,,	− 34
< ·001 ,,	...	22 ,,	− 34·5

It will be seen from the above table that at the end of three hours' constant pumping by the Gaede pump the pressure of the air in the apparatus had fallen very low, and that the rate of charging of the polonium had become constant before the magnetic field was applied.

Immediately after the readings on the rate of charging of the polonium with increasing magnetic fields were taken, another reading was taken of the rate of charging of the polonium without the magnetic field. After this the brass plate was cooled by pouring liquid air in the tube E, and the readings on the rate of charging of the polonium were continued once more.

TABLE XV.

Air in Apparatus.

Brass Electrode. Voltage on Brass = −81 volts.

Pressure of air in apparatus.	Time from initial reading of Table XIV.	Current through magnet.	Current to polonium.
<·001 mm.	28 min.	0 amp.	−238·5
Cooled Brass with Liquid Air.			
·003 mm.	35 min.	0 amp.	−235·5
·005 „	40 „	0 „	−227
·005 „	50 „	0 „	−217
·005 „	65 „	0 „	−214
·004 „	80 „	0 „	−210·5
·004 „	95 „	0 „	−210·5
·004 „	110 „	0 „	−210·5
·003 „	140 „	0 „	−209
·003 „	170 „	0 „	−210·5
·003 „	...	1 „	− 42·5
·003 „	...	9·5 „	− 35·6
·003 „	...	16 „	− 35·6
·003 „	...	21·5 „	− 36·5

From the numbers given in the table it will be seen that immediately after the brass began to cool down to the temperature of the liquid air the pressure in the apparatus rose slightly and then fell again as the pumping was continued. The rate at which the polonium charged up, however, steadily decreased as the brass plate cooled down. As the effect of a rise in pressure would be to increase the ionization current in the chamber, it follows from the occurrence of this decrease in the rate of charging of the polonium that the secondary radiation from the brass plate must have dropped off as its temperature lowered.

The values of the α ray excited secondary radiation from the brass plate at temperatures 20° C. and −192° C. as deduced from Tables XIV. and XV. are given in Table XVI.

Table XVI.

Brass in Air.

Secondary Radiation from Brass and Air Layer.

Temperature of Brass	20° C.	−192° C.
Secondary Radiation...............	−215	−173

From the numbers given in the table it is evident that the secondary radiation from the brass at a temperature of 20° C. was about 25 per cent. higher than it was under the same α ray bombardment at the temperature of liquid air.

If differences in α ray excited secondary radiation at low pressures be taken to connote differences in the quantities of gas occluded at the surface of the substance bombarded, the meaning of this smaller secondary radiation from the brass at liquid air temperature is that the brass held less gas in its surface at liquid air temperature than at the temperature of the room. This experiment therefore strongly supports the explanation given above of the greater difficulty experienced in pumping the air from the brass chamber at −192° C. than in making the same exhaustion when the apparatus was maintained at the temperature of the room.

5. *Summary of Results.*

1. The secondary radiation excited by the α rays of polonium in carbon was found to increase in intensity as the temperature of the carbon was lowered from room temperature to the temperature of liquid air.

2. This increase in the secondary radiation from carbon as its temperature was lowered has been shown to be due to an increase in the amount of gas occluded in the surface of the carbon.

3. Since it has been shown that gases occluded in such substances as carbon contribute to the secondary radiation excited at the surface of these substances by α rays, it follows that the procedure adopted in this investigation constitutes a new method of studying the phenomena of occlusion.

4. The results of the experiments described in this paper also go to show that with a metal like brass the amount of a gas retained in its surface when it is placed in a vacuum is less at the temperature of liquid air than at ordinary room temperature.

In conclusion, I desire to thank Professor McLennan for the kindly interest he has shown throughout the course of this research.

XXXVI. *On some Applications of the Law of the Rectilinear Diameter.* *By* H. Davies, *B.Sc., Head of Physics Department, Municipal College, Portsmouth* *.

THE law of the rectilinear diameter was published by Cailletet and Mathias † in 1886. With temperatures as abscissæ and densities as ordinates, they plotted a curve including liquid and vapour densities up to the critical point. The two branches merged into one another at the critical point. The points of mean density were found to lie on a straight line. The mean density is then a linear function of the temperature and can be expressed as

$$D_l + D_v = a - bT,$$

or

$$D_l + D_v - 2D_c = c(T_c - T).$$

S. Young ‡ has shown that there is a slight departure from linearity, and adds a term containing $T_c^2 - T^2$ as a small correction to the right-hand side of the second expression. In a previous note § the author has shown from the first expression that the coefficient of expansion of a liquid is closely related to the critical temperature. Some further relations are obtained in the present paper by the use of this principle. In the first two sections the value of K is taken instead of n^2, owing to the difficulty of access to values of n^2 for infinite wave-length without much laborious calculation.

1. *On the Ratio of the Volume at the Absolute Zero of Temperature to the Real Volume of the Molecules in a Unit Mass.*

Stefan ‖, in his memoir on the theory of diffusion of gases, drew attention to a simple relation between the refractive index of a gas and the mean free path of the molecules. He gave the relation in the form $(n-1)L =$ constant. Clausius ¶ developed the idea on the lines of Maxwell's and Helmholtz's theories, and showed that the expression $\frac{K-1}{K+2}$ represents the ratio of the real volume of the molecules of a substance to the volume they actually occupy, K being the specific inductive capacity. Mosotti and Exner [*] further developed the idea with reference to the equivalent expression $\frac{n^2-1}{n^2+2}$, n being the refractive index which on Maxwell's theory is equal to $\sqrt{K}$. Proceeding from Clausius's expression it is possible to obtain the value of the ratio of the volume at the absolute zero of temperature to the real volume of the molecules. Let V, V_0, V_l, and V_c be the absolute volume, the volume at the absolute zero of temperature, the volume of the liquid at temperature T (abs.), and the critical volume respectively, of a unit mass of a substance. Further, let $V_0=k\,.\,V$.

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* Communicated by Prof. A. W. Porter, F.R.S.

† *Comp. Rend.* cii. 1886.

‡ Phil. Mag. (5) 1900, p. 291.

§ Phil. Mag. April 1912.

‖ *Wien. Sitzungsber.* lxv. (1872).

¶ *Mechanische Wärmetheorie,* 1879.

From the law of the rectilinear diameter of Mathias it has been shown that for liquids sufficiently far removed from their critical temperatures [†]

$$D_l = 2D_c\left(\frac{2T_c-T}{T_c}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$= \frac{2D_c}{\alpha T_c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where α is the coefficient of expansion and is equal to

$$\frac{1}{2T_c-T}\ddagger.$$

In obtaining the above result use was made of Guldberg's [§] result that $D_0=4D_c$. Using this in equation (1) it follows that

$$D_l = \frac{D_0}{2\alpha T_c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The ratio of the volume at the absolute zero to the absolute volume is given by $V_0=kV$, and on substituting in (2) it follows that

$$\frac{V}{V_l}=\frac{1}{2\alpha k T_c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This must be equal to the expression given by Clausius, and therefore

$$\frac{K-1}{K+2}=\frac{1}{2\alpha k T_c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence

$$\frac{K+2}{K-1}\cdot\frac{1}{2\alpha T_c}=k. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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[*] *Wien. Ber.* xci. p. 850 (1885).

[†] Phil. Mag. April 1912.

[‡] Ibid.

[§] Guldberg, *Chem. Centr.-Bl.* vol. ii. p. 1042 (1898).

The values of k for a series of liquids for which Maxwell's relation $K=n^2$ approximately holds is given in Table I. below.

TABLE I.

Liquid.	K.	a.	T_c.	k.	Diff. from Mean.
Benzene	2·3	·001176	563	2·499	−·001
Carbon bisulphide	2·62	·00114	575	2·291	−·201
Carbon tetrachloride	2·25	·001186	558	2·56	+·06
Cymene	2·25	·000895	652	2·68	+·18
Toluene	2·375	·00107	594	2·5	......
Thiophene	2·76	·0011	590	2·3	−·2
Turpentine	2·3	·0009	649	2·59	+·09
Naphthalene	2·7	·000747	741	2·498	−·002
Xylene-o	2·567	·00095	631	2·432	−·068

Mean value = 2·5

These liquids were selected quite at random from Landolt and Börnstein's tables, and the value of k comes out with very satisfactory consistency. The mean value 2·5 is regarded for the remainder of the paper as the value of the ratio of the volume at the absolute zero of temperature to the real volume occupied by a given number of molecules.

2. *Inductive Power and Molecular Inductive Power.*

The Lorenz-Lorentz expression

$$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d} \quad \text{and} \quad \frac{n^2-1}{n^2+2}\cdot\frac{M}{d}$$

are known as the "refractive power" and the "molecular refractive power" respectively, M being the molecular weight. It seems appropriate, therefore, to give the names "Inductive Power" and "Molecular Inductive Power" to the corresponding expressions when K is used.

From equations (1) and (4)

$$\begin{aligned}\frac{K-1}{K+2}\cdot\frac{1}{d} &= \frac{1}{2\alpha k T_c}\cdot\frac{1}{\frac{2D_c}{\alpha T_c}}\\ &= \frac{1}{4kD_c}\\ &= \frac{V_c}{10}. \qquad \ldots\ldots\ldots \quad (6)\end{aligned}$$

The inductive power is thus a constant and numerically equal to one tenth of the critical volume. The molecular inductive power given by $\frac{K-1}{K+2} \cdot \frac{M}{d}$ will obviously reduce to the same expression if V_c is the critical volume of a gramme-molecule. Table II. shows the values of the molecular inductive power and one tenth the critical volume for a few liquids.

TABLE II.

Liquid.	Molecular Inductive power.	$\frac{V_c}{10}$.
Benzene	26·79	26·1
Ether *	34·1	34·3
Carbon bisulphide	22	24
Carbon tetrachloride	26·7	27·6
Toluene	33·54	34·5
Naphthalene	40·2	39 6

* Value of K for Ether is 2·12 at 180° C. This value was adopted for calculation.

The agreement here is quite satisfactory, only carbon bisulphide being 10 per cent. out.

3. *Molecular Inductive Power and Critical Coefficient.*

Relationships should exist between molecular inductive and refractive powers and the critical constants. Guye † showed that for some gases and liquids the molecular refractive power is 1·8 times the critical coefficient $\frac{T_c}{P_c}$.

No theoretical basis has hitherto been published—so far as the author is aware—for this relationship. One can be obtained as follows. Prof. Young has calculated for many substances the ratio between the ideal critical volume and the actual critical volume. He defines the ideal critical volume as the volume which the substance would occupy at its critical temperature and pressure if it was an ideal gas. The values he obtains have as their mean 3·7. Let V_c' be the ideal critical volume. Then

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† Guye, *Ann. Chem. Phys.* (6) xxi. p. 222 (1890).

$$V_c' = R\frac{T_c}{P_c}. \quad \dots\dots\dots \quad (7)$$

Also $$V_c' = 3{\cdot}7\,V_c.$$

Then $$V_c = \frac{R}{3{\cdot}7}\cdot\frac{T_c}{P_c}. \quad \dots\dots\dots \quad (8)$$

Substituting in (6), the molecular inductive power

$$= \frac{K-1}{K+2}\cdot\frac{M}{d} = \frac{R}{10\times3{\cdot}7}\times\frac{T_c}{P_c}$$

$$= \frac{8{\cdot}32\times10^7}{10\times3{\cdot}7\times1{\cdot}014\times10^6}\times\frac{T_c}{P_c}$$

$$= 2{\cdot}3\frac{T_c}{P_c}. \quad \dots\dots\dots\dots \quad (9)$$

P_c is here measured in atmospheres. The molecular inductive power therefore has a constant ratio of 2·3 to the critical coefficient. In Table III. following the values of the molecular inductive power, the critical coefficient, and their ratio is shown for a number of liquids.

Table III.

Liquid.	Molecular Inductive Power.	$\frac{T_c}{P_c}$.	M.I.P. $\div\frac{T_c}{P_c}$.
Benzene	26·79	10·42	2·56
Carbon bisulphide	22	7·4	2·7
Carbon tetrachloride	26·7	9·9	2·6
Cymene	45·24	21·28	2·13
Toluene	33·54	14·28	2·29
Naphthalene	40·2	18·8	2·18
Xylene-o	47·6	18	2·6
Aniline	30·27	13·4	2·4

Mean... 2·43

The mean value of the coefficient for the eight liquids given is 2·43, which is just 5 per cent. above the theoretical value. When the uncertainty of T_c, P_c, V_c, and K as given in the tables—in some cases differences of 10 to 20 per cent. occur for the values obtained by different observers—is taken into account the agreement is satisfactory enough. Although all the above liquids approximately obey Maxwell's law, it is probable that the values of K are higher than the best modern determinations would give for them.

4. *The Co-volume and Intrinsic Pressure of Liquids.*

The term $(v-b)$ in the various equations of state is termed the co-volume. Further, "b" is the volume at the absolute zero of temperature. Taking, as in my previous paper, Guldberg's value for the ratio of the density at absolute zero to the critical density as 4, it follows that $b=\frac{1}{4} . V_c$. Again, from $(1a)$ above

$$D_l = \frac{2D_c}{\alpha T_c},$$

whence

$$V_l = \tfrac{1}{2}\alpha T_c . V_c.$$

The co-volume is consequently given by

$$\begin{aligned} v_l - b &= \frac{V_c}{4}(2\alpha T_c - 1) \\ &= \frac{V_c}{4}\left(\frac{2T_c}{2T_c - T} - 1\right) \\ &= \frac{V_c}{4}\alpha T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

Since $b = \frac{V_c}{4}$. This immediately gives

$$v_l = b(1+\alpha T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If α were constant this would be the ordinary linear relation between v_l and T; but it must be remembered that α is a function of T. The equation of state for a liquid can be written in the form

$$(p+\pi)(v-b) = RT,$$

where p is the external and π the internal or intrinsic pressure. If p is neglected in comparison with π and $(v-b)$ written as ϕ the equation becomes

$$\pi\phi = RT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

On substituting the value of ϕ from (10) it follows that

$$\pi = \frac{4R}{\alpha V_c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This equation enables π to be calculated from the known values of v_c, α, and R. Substituting for α its value $\frac{1}{2T_c-T}$ we get

$$\pi=\frac{4R}{v_c}(2T_c-T)$$

$$=\frac{8RT_c}{v_c}\left(1-\frac{T}{2T_c}\right) \quad . \quad . \quad . \quad . \quad (14)$$

The value of π at the absolute zero is thus given by $\frac{8RT_c}{v_c}$. If Young's value of the ratio of the ideal to the actual critical volume is taken this reduces at once to $29{\cdot}6\, P_c$. Apparently π should vanish at the temperature $T=2T_c$. The formula can, however, only be approximate as p approaches P_c. An estimate of the error can be obtained by placing $T=T_c$ and assuming π to include the external pressure (which is not negligible under the conditions which would then hold). We then obtain $\frac{\pi_c v_c}{RT_c}=4$, while the experimental value is 3·7.

From (14) the temperature variation of π is at once obtained. Thus

$$\frac{d\pi}{dT}=-\frac{4R}{v_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$=-\frac{R}{b} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$=-14{\cdot}8\frac{P_c}{T_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The relation expressed in (17) is obtained from (15) by means of the equation (8).

If (15) is divided by (13) we obtain

$$\frac{1}{\pi}\cdot\frac{d\pi}{dT}=-\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This is a very simple relation. The above values of π and $\frac{d\pi}{dT}$ are quite new and give the means of calculating them for any liquid for which the critical data are available. In cases for which v_c is not given, equation (13) can, by using (8), be put in the form

$$\pi=14{\cdot}8\frac{T_c}{\alpha\,.\,P_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The calculations for the tables below were based on the experimental results given in Landolt and Börnstein. The coefficients of expansion were calculated for 15° C. Where experimental values were not given they were calculated from $\alpha = \frac{1}{2T_c - T}$ for $T = 288$. The table gives the values of π, ϕ, and $\frac{d\pi}{dT}$; π is in atmospheres, ϕ in c.c. per gram. molecule.

TABLE IV.

Liquid.	π.	ϕ.	$\frac{d\pi}{dT}$.
Acetone	1268	18·54	−1·74
Ether	778·9	39·1	−1·25
Ethylamine	1328	17·8	−2·17
Ethyl benzene	863·2	34·43	− ·91
Ethyl alcohol	1348	17·6	−1·81
Aniline	1176	19·2	−1·11
Benzene	1102	21·45	−1·31
Mono. chor. benzene	1027	22·97	−1·05
Carbon tetrachloride	1076	21·96	−1·3
Cymene	661	35·8	− ·65
Diethylamine	838·5	28·15	−1·2
Methyl ether	1082	21·8	−2·1
Naphthalin	935	31·8	− ·783
Pentane	677	28·7	−1·04
Propyl alcohol	1127	21	−1·43
Carbon bisulphide	1683	13·95	−2·08
Toluene	1188	25·05	−1·036
Tri-ethylamine	649	40·7	− ·83
Xylene-o	845	27·96	− ·87

A discussion of the various methods which have been proposed for the calculation of π has been published by Dr. Lewis *. The only methods to which reference need be made here are to those of Benedicks †, Traube ‡, and Lewis *.

Benedicks calculates π from a relation $\pi = \frac{R}{v\alpha}$ which he obtains from Van der Waal's equation. This is very similar to (13) above. The values of π obtained from this relation will be very much the same as from (13), since in liquids "v" and "b" $\left(i.\ e.\ \frac{v}{4}\right)$ are of the same order of magnitude.

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* Phil. Mag. July 1911, pp. 193–197.

† *Zeit. für anorg. chem.* xlvii. p. 455 (1905).

‡ *Ibid.* xxxiv. p. 416 (1903).

Traube has proposed a method to which Lewis does not refer. From considerations of the refractive index he arrives at the conclusion that the co-volume of all liquids at the same temperature and pressure is 24·5 c.cm. per gramme molecule, and thence obtains π from $\frac{22{,}400}{24{\cdot}5} = 970$ atmospheres. The co-volume, however, is not constant by any means, and consequently the method fails. It must be noted though that 24·5 is very near to the mean value of my determinations, which is 25·67 c.cm. It should be noted also that all the above figures relate to liquids which are not at all, or very slightly, associated.

Lewis deals very fully with the Dupré relation between π and the internal latent heat of vaporization. He shows that a better result would probably be obtained from a relation of the form

$$\pi = l + \mathrm{T}\frac{d\pi}{d\mathrm{T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where l is the latent heat per unit volume, but he made no calculations as no information was available with regard to $\frac{d\pi}{d\mathrm{T}}$.

If in (20) we supply $\frac{d\pi}{d\mathrm{T}}$ from either (15), (16), or (17) we get

$$\pi = l - \mathrm{T}\,.\,\frac{4\mathrm{R}}{\mathrm{V}_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$= l - \frac{\mathrm{R}}{v}.\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$= l - 14{\cdot}8\frac{\mathrm{P}_c}{\mathrm{T}_c}.\,\mathrm{T}. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Either of the above forms will enable the necessary calculations to be made from data for l and the critical constants of the substance. The actual values of $\frac{d\pi}{d\mathrm{T}}$ are given in column 4 of Table IV. The values of π obtained from (21) for a few liquids are shown below with those from Table IV.

TABLE V.

Liquid.	π (21).	π (13).
Benzene	912	1102
Toluene	1042	1188
Aniline	1315	1176
Cymene	686	661

If in equation (20) use is made of (18) we get

$$\pi = l - \alpha\pi\mathrm{T},$$

whence

$$\pi = \frac{l}{1+\alpha\mathrm{T}} \quad \ldots\ldots \quad (24)$$

$$= \frac{l}{1+\dfrac{\mathrm{T}}{2\mathrm{T}_c-\mathrm{T}}}$$

$$= \frac{l}{2\alpha\mathrm{T}_c} \quad \ldots\ldots \quad (25)$$

This equation should be practically equivalent to (20).

In this paper only liquids which are not associated have been considered. I hope to deal with associated liquids in a future paper.

In conclusion I wish to express my warmest thanks to Prof. Porter for his corrections and suggestions and for the kindly interest he has taken in my work.

XXXVII. *On the Spread of the Discharge from an Electrified Point.* By A. M. TYNDALL, *D.Sc., M.Sc., Lecturer in Physics in the University of Bristol* *.

THE following experiments were originally undertaken with the view to test the hypothesis that there is in discharge between a point and a plane at atmospheric pressure, a back discharge from the plate which is negligible in amount only for very small currents. It has been found, however, that the method employed does not give definite evidence for or against the hypothesis for reasons stated below; but the results are not without interest, and they are therefore here described.

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* Communicated by the Author.

That point discharge at atmospheric pressure and moderate currents is not solely a one-way discharge has been suggested by various experimenters. Thus Campbell[*] has shown by the condensation method that negative ions are present during positive discharge. Secondly, the author[†] found that there is an apparent increase—when the current increases—of the specific velocity of the ions in air, as measured by the wind-pressure method; this is readily explained by back discharge. The discharge has since been examined under better conditions, and it has been found that at the currents at which this effect is appreciable the whole discharge region is very faintly luminous. Thirdly, there is definite evidence[‡] for back discharge in exceedingly pure hydrogen, since in the purest samples of that gas the direction of the electric wind is actually from plate to point.

On the other hand, Zeleny concludes from some experiments on the rate of leak of a charged conductor placed in the discharge, that back discharge, if present, is exceedingly small in hydrogen and air at atmospheric pressure.

Recently, Moore[§] has shown that calculating the velocity of the ions from the reaction at a discharging point, on the assumption of one-way discharge, values are obtained about five times greater than those generally accepted. He points out that this may be explained either by the presence of discharge from the plate or of a region of ionization extending some distance from the point. That the nature of the discharge within a few millimetres of a point is different from that beyond that distance has been shown in the various measurements of the electric wind. It is not necessary, therefore, to suppose a general back discharge to explain his results.

The method of investigation in the present work depends upon some observations made by Chattock[||], who found that the area over which the current spreads is slightly greater in negative than in positive discharge. Assuming that back discharge is absent, or at any rate small, this leads to a simple method of comparing the specific velocity of ions under different physical conditions. If this method be tested for a known case and it be found that the calculated value is different from that generally accepted, there would be strong indirect evidence that the assumption of one-way flow is not justified. The method is as follows:—

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[*] Campbell, Phil. Mag. vol. vi. p. 618.

[†] Phil. Mag. vol. xxi. p. 585 (1911).

[‡] Chattock & Tyndall, Phil. Mag. vol. xix. p. 449 (1910).

[§] Phys. Rev. Feb. 1912.

[||] Phil. Mag. vol. xlviii. p. 401 (1899).

Consider a given charged point opposite an earthed plate. When no discharge is occurring the distribution of lines of force between them is settled by the potential of the point. When discharge is occurring, the distribution is changed owing to presence of free ions in the space between the electrodes, the amount of change depending upon the current passing from point to plate. Suppose that without altering the geometrical conditions it were possible to double the electrical density at every point on the electrodes. It seems to follow as a necessary consequence that in doing this the volume density of the ions at every point would also be doubled, assuming that the magnetic effect of the moving ions has no appreciable influence on the general ionic distribution. (A simple calculation shows that this assumption is quite justified even close by the point where the ionic velocities must be high.)

A given ion under these conditions will still travel along the same path as before, but owing to the change of density of charge, the potential gradient at every point will be doubled, and the ion will move at double the rate, thus contributing double the current to the plate. Since, also, the volume density of the ions is doubled, the current at any point on the plate will be in all increased four times. In other words, for a constant relative distribution of the field—referred to in future as a "constant spread," the current C at any point on the plate is given by

$$\frac{C}{V^2} = \text{constant},$$

where V is the difference of potential between point and plate. This formula only applies for given ions under constant physical conditions. If by varying the conditions the specific ionic velocity of the ions "v" is changed, then

$$\frac{C}{V^2} \propto v.$$

To test this expression the following apparatus was set up:—The plate, 15 cm. in diameter, consisted of a central brass disk A surrounded by concentric brass rings B, C, and D, all insulated from one another and supported on ebonite pillars fixed to a large disk forming the lid of a bell-jar. Through the neck of this bell-jar was the sliding point P, backed by a plate, also adjustable in position. A galvanometer, suitably shunted, was connected to each of the zones A and C, the zones B and D being earthed directly. In some of the work a galvanometer was connected to each zone, so that simultaneous observations might be made on the current at different parts of the plate; and the total current arriving at the plate was also measured by a galvanometer placed between the other galvanometers and the earth. The bell-jar was filled with dry air at atmospheric pressure.

The electrometer used to measure the potential of the point was of an attracted disk type, used originally by Chattock *. In it the attracted disk is suspended, and the force of attraction measured by tilting the whole instrument until the disk falls back by its own weight to a fixed point; a fine glass pointer attached to the back of the disk and viewed through a microscope serves as an indicator. By altering the distance between the attracting plate and the suspended disk the range of the instrument can be varied from about 100 volts to some tens of thousands.

The spots of light of the two galvanometers connected to A and C were made coincident upon the same scale, and the Wimshurst was turned at such a rate that the deflexions of the two galvanometers were equal. Similar readings were then taken for the other sign of discharge, though the value of the deflexion common to both instruments was now different. Since the ratio of the currents at the two areas A and C was the same in both cases, the necessary condition of constant spread was thus attained. From the current and potential readings the ratio of the specific velocities of the positive and negative ions in air at atmospheric pressure was then calculated.

Some typical results are given in the following table in which d is the distance between point and plate, and r the ratio of the specific velocities of negative and positive ions in air.

TABLE I.

d (in cms.).	r.
1·4	(1·49)
2·4	1·38
4·4	1·38
6·4	1·41
8·4	1·39
9·4	1·40
Mean	1·39

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* Phil. Mag. [5] vol. xxxii. p. 302 (1891).

While maintaining "constant spread" it was not possible to vary the current more than about 100 per cent. Within these limits, however, *r* was independent of current; the above values are mean values.

The mean value which, omitting the first reading, is 1·39, is in agreement with that obtained by recognized methods, namely about 1·37, when, as in the above work, no refined process of drying of the air has been employed.

Now there are two assumptions made in the above treatment: (*a*) that there is no back discharge from the plate, and (*b*) that the starting conditions close to the point are the same for both signs of discharge.

It is not possible to calculate the effect of back discharge on the distribution, but it is probable that the presence of a small amount of back discharge in *both* signs of discharge would have little effect upon the value of *r* obtained. The rise of *r* at short distance (see Table I.) might be taken as evidence of a strong back discharge under these conditions were it not for the probability that at these distances the assumption (*b*) breaks down.

The different appearance of the glow at a positive point to that at a negative, the modified nature of the discharge within a few millimetres of the point, as shown by the electric wind measurements and the recent experiments of Moore, all lead to the conclusion that the conditions close to the point are different from those further away. These may well differ in the two signs of discharge. For short distances between point and plate this difference is sufficient to introduce an inaccuracy in the ratio *r*, though it appears negligible for the greater distances.

The results may therefore be explained without assuming any back discharge to be present. On the other hand, the fact that *r* is correct in cases where the discharge region was faintly luminous makes it possible that it is present in small quantities in both signs of discharge without affecting the relative distribution of current in the two cases.

The breakdown of one or other of the assumptions (*a*) and (*b*) makes it impossible to apply the method to different pressures. Thus the pressure was varied from atmospheric down to 10 cm.: within these limits the product of the mobility (v) and pressure (p) should be constant. Readings were taken of constant spread at various pressures, one of which was atmospheric, and the values of rp obtained in terms of its value at atmospheric pressure taken arbitrarily as 1·00. These are shown in Table II. for positive discharge. Similar effects were obtained with a negative point.

TABLE II.

v.	*vp.*
75·5	1·00
55	·98
40	·90
30	·82
20	·74
10	·64

It will be seen that the deviation from $vp=1{\cdot}00$ increases with fall of pressure, but whether this is due to an extension of the region of modified discharge or to a marked setting in of back discharge cannot be stated. At any rate the method as one for comparing specific velocities under varying physical conditions is not satisfactory, since in the case of varying pressure it breaks down entirely.

Effect of Discharge from the Plate.

It was shown by the author[*] that in certain cases there was a marked change in the character of the electric wind as the distance between point and plate was increased, the pressure of the wind in each case falling short of that anticipated from theory. The effect, since it was accompanied by a speck of light upon the plate, was no doubt due to a back discharge from this speck which contributed to the current but which gave a wind effect opposed to that of the main discharge.

With the above apparatus some idea of the magnitude of this effect could be obtained by observations on the current arriving at each zone of the plate.

In order that the speck of light on the plate could be obtained under controllable conditions it was made to occur at a fine point N, which could be projected at will through the zone A of the plate to the extent of a millimetre or so.

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[*] Phil. Mag. vol. xxi. p. 585 (1911).

The results are shown in Curves I. and II. Curves I. are for positive discharge, and in them the currents arriving at A, B, and C are plotted as ordinates with the total current arriving at the plate as abscissæ (circles). The curves with crosses give the results when no point was projecting, and hence no glow present. Curves II. give the curves for negative discharge under the same conditions. Glow was observed to start at 10 microamperes for positive, and at about 12 m.a. for negative discharge. The ordinates are in arbitrary units.

It will be seen that particularly in positive discharge there is a marked rapid increase in the current between P and A after glow has started at N.

Both the glow and the increase in current set in much more gradually in negative discharge. This is readily explained if, when N is negative, it is more efficient as a source of back discharge than when it is positive.

For a given current flowing, the current at B, C, and D after glow has started at A, must be less than the current at these when no glow is present. This is also shown in Curves I. and II., the Curves for B and C alone being plotted. The main part of the increase in current passes between the two points.

Moreover, it was previously observed that with increasing current the distance between point and plate when the character of the wind changed decreased. In the present work it was found that the current at which glow appeared also increased as the distance between point and plate decreased. This was to be expected if the glow made its appearance at a certain critical value of the field near the plate.

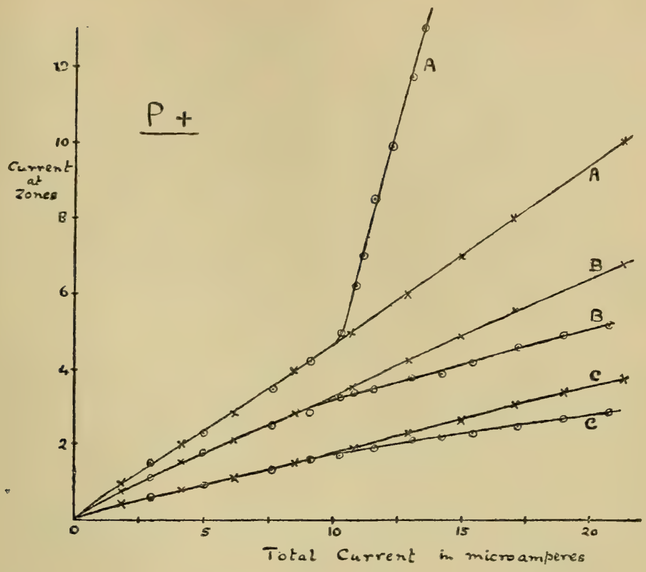
That the presence of the projecting point has no effect upon the geometrical conditions is shown by the fact that the distribution of current over the plate, before glow, is the same whether the point is there or not.

Lastly, the apparatus was used to clear up another question outstanding from previous work.

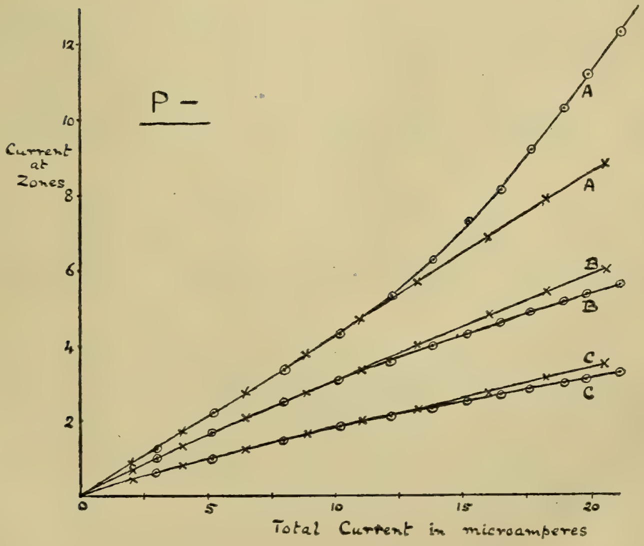
It was found * that in very pure hydrogen the plate was covered by a velvety glow which underwent curious fluctuations in size, sometimes extending over the whole plate and sometimes contracting to the size of a threepenny piece; the changes were in all cases rapid and irregular. This was discussed in the light of the back discharge which the wind measurements showed to be present in that gas.

* Chattock & Tyndall, Phil. Mag. vol. xix. p. 449 (1910).

Curve I.



Curve II.



By simultaneous observations on the current at each zone of the plate described above, it was possible to test whether similar effects were present in air, but had not been previously detected owing to the absence of a glow at the plate. Thus any contraction of the area of discharge (corresponding to a contraction of the glow in the case of hydrogen) would be shown by a sudden increase of the deflexions of the galvanometers connected to the inner zones and a sudden diminution in deflexion of those connected to the outer zones when the total current was maintained constant. No such effect in air was observed. Also when fluctuations of the total current occurred they were invariably accompanied by fluctuations of the same sign at each zone simultaneously.

Summary.

A method of comparing the specific velocity of ions under different physical conditions, from the distribution of current over the plate in point-plate discharge, has been tested for the ions in air.

The observed ratio of velocities of these ions at atmospheric pressure agrees with the accepted value. Owing, however, to the breakdown of assumptions as to the nature of the discharge the method cannot be applied to lower pressures, and for the same reason has probably only a restricted application in general.

In the light of these results the question of the presence of a discharge from the plate is discussed, with the conclusion that though certain facts strongly point to its presence, it is not necessary to the explanation of the above work. Finally, certain special cases of discharge from the plate met with in earlier work have been further investigated.

XXXVIII. *A Comparison of the Ionization within closed vessels due to Röntgen and Gamma Rays.* *By* A. S. Eve, *D.Sc., McGill University, Montreal* *.

If closed cylindrical vessels, made of various metals, equal in height and diameter, and with walls about half a millimetre thick, are exposed to the action of Röntgen rays and of the γ rays from radium C respectively, then the results obtained give a comparison of the ionizing effects of the two types of rays.

The results are at first sight surprising.

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* Communicated by the Author.

Ionizations.

Metal.	Thickness.	Density.	X Rays.	γ Rays.	Atomic weight.
Lead	2·1 mm.	11·3	1·8	100	207
Copper	·54 ,,	8·9	82	69	63·6
Zinc	·44 ,,	7·1	111	69	65·4
Iron	·55 ,,	7·8	100	68	55·9
Aluminium ...	·60 ,,	2·6	126	58	27·1
Cardboard	...	...	125	49	

It will at once be seen that with Röntgen rays the heavier metals permit of less ionization, within the testing vessel, than do the lighter metals. But with γ rays the metals with the higher atomic weight give rise to stronger ionization, within the vessels, than do those with lower atomic weight.

Experimental Details.

Three different methods were employed and these gave, broadly speaking, concordant results.

(1) A very thin-walled electroscope, supported on light pillars, was covered in turn with cylinders, having the upper end closed, made of the metals named above. After taking the initial reading the electroscope was covered with the inverted vessel and exposed for a known time to the action of X or γ rays. The vessel was then removed and the fall of potential determined.

(2) An axial rod was placed in turn within the cylindrical vessels, and this rod was connected to a small electroscope above a lid covering the vessel.

(3) Inverted cylinders, 30 cm high, 17 cm. in diameter, were placed in turn on the upper platform of the well-known Wulf electrometer. The long axial rod, about 30 cm., sold with the instrument, was charged initially to 200 volts, and the fall of potential due to the respective rays was measured and the natural leak deducted.

For the γ rays 14 mg, of pure radium bromide in a test-tube was placed within a lead cylinder, 6 mm. thick, between the poles of a powerful electromagnet. In this way the β rays from the radium were absorbed and the emergent β rays due to the γ rays passing through the lead cylinder were for the most part deflected from the electroscope which was a metre and a half away.

The results given below to an arbitrary scale, without and with the magnetic field, show the necessity for this precaution.

	No magnetic field.	Magnetic field.
Pb	11·1	10·9
Cu	7·8	7·6
Zn	8·0	7·6
Fe	7·6	7·5
Al	7·1	6·3
Cardboard...........	7·0	5·3

The Röntgen rays came from a rather hard bulb (λ in air equal to ·0004 cm.$^{-1}$), and it was necessary to cut down the intensity of the rays by a plate of lead 1·8 mm. thick placed near the bulb, which was six metres from the electroscope. The time of exposure was governed by a control electroscope.

Experiments were also made with softer rays, and the results may be contrasted, iron in each case taken as standard.

	Thickness.	Soft X Rays.	Hard X Rays.	Hard × thickness × density.	Hard × thickness × atomic weight.
Pb	2·1 mm.	small	1·6	195	780
Cu	·54 „	68	82	430	2810
Zn	·44 „	121	111	345	3190
Fe	·54 „	100	100	393	3080
Al	·60 „	238	126	400	2080
Cardboard ...	...	...	125		

It was necessary to make the lead vessel fairly thick (2·1 mm.) in order to secure rigidity. It was three or four times as thick as the other vessels. The high values for zinc are in part due to its relative thinness.

Discussion.

The problem appears to be too complex for reduction to a simple formula. It is, however, possible to give a satisfactory general explanation of the results, and to show that the ionization effects obtained are not out of harmony with the view that X and γ rays are similar in type.

The explanation is derived from Bragg's theory of the nature of the ionization produced by Röntgen and γ rays, and from the remarkable experimental verification obtained by C. T. R. Wilson by photographs of ionization effects in an expansion-chamber.

In the case of Röntgen rays, ionization appears to be due to the expulsion of electrons from air or other substances, and these electrons, having paths about a millimetre in length, produce groups of electrons along those paths.

In the present experiments the testing vessels cut down the intensity of the Röntgen rays to an extent mainly dependent on the thickness and density of the walls. The electrons are projected from the air and from the walls, with velocities of the order 10^9 cm. sec.$^{-1}$, and have irregular paths about a millimetre in length. Hence there is least ionization with thick or heavy walls which cut off the primary and secondary Röntgen rays, and prevent them from causing volume ionization of the air within.

But with γ rays the ionization is mainly due to the electrons with much higher velocity expelled by or from the γ rays, chiefly on meeting the walls of the vessel. These electrons have velocities of the order of those of the β rays from radium C, 10^{10} cm. sec.$^{-1}$, with an average path of one or two metres. Moreover, many electrons, before absorption, will be reflected again and again from the sides of the vessel, ionizing the air along their paths.

The extent of ionization due to multiple reflexion may be gauged from the results of Kovarik*, who experimented with β rays striking reflectors above and below his testing vessel.

Ionization Measurements.

	Kovarik. β rays with multiple reflectors.	Testing vessels and γ rays.
Pb	100	100
Zn	70·5	69
Cu	69·5	69
Fe	65·0	68
Al	51	58
Cardboard............	42	49

The agreement between his results for β rays and my results with γ rays is sufficiently good to indicate that multiple reflexion of the secondary β rays, originating at the walls when the γ rays strike them, is the principal cause of the ionization within the testing vessels The effect is controlled by the atomic weight of the material of the walls of the vessel.

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* Phil. Mag. November 1910.

Moreover, the γ rays which strike the concave or further side of the vessel produce "incident" β rays to an extent also dependent on the atomic weight.

But as Bragg has shown, this is not the case with the "emergent" secondary radiation arising on the convex side where the γ rays first strike. In this case the ionization plotted against the atomic weight gives a U-shaped curve, so that aluminium is about equal to lead as an ionizer.

So far as the "emergent" electrons are concerned, we might expect an aluminium vessel to give as much ionization as a lead vessel, with penetrating γ rays and suitable thickness of walls. But such a result would be difficult or impossible to realize, because the "incident" radiation and the multiple reflexion together quite overwhelm and mask this emergent radiation effect.

The influence of the thickness of the walls is not very pronounced in the case of the γ rays; but of course very thin or very thick walls alike give small results. The curve, ionization plotted against thickness, rises rapidly from the origin to a maximum and proceeds with a slow decrease, and is represented by the difference of two exponentials.

The results obtained then agree well with the view that the Röntgen rays ionize mainly or wholly by electrons projected with velocities of the same order as those of the cathode rays; and that the γ rays from radium C also ionize mainly or wholly by electrons projected with velocities of the same order as those of the β rays from radium C.

With the X rays these electrons originate chiefly in the air in the testing vessel, but with the γ rays for the most part from the walls.

Some experiments made with very thin-walled electroscopes indicated that with Röntgen rays the ionization within iron or zinc vessels about half a millimetre thick is only 15 or 16 per cent. of that in the free air.

But with γ rays the ionization in such vessels is about 140 per cent. of that in the free air. The experiments in each case were made in the centre of a fairly large room with brick walls.

McGill University, Montreal,
June 15, 1912.

XXXIX. *On the Theory and Measurement of Residual Charges.* *By* Prof. A. Anderson, *M.A., and* T. Keane, *B.A.*[*]

THE following attempt to throw light on the action in a dielectric which results in a residual charge is based on Maxwell's treatment of the subject. He pictured the medium as varying from point to point, both in specific inductive capacity and in specific resistance, and worked out the solution for the case of a dielectric of lamellar structure in which there were discontinuities in the values of these quantities at the bounding surfaces. The case of a single dielectric between two parallel plate electrodes, in which the specific inductive capacity and specific resistance are finite and continuous functions of the distance from one of the plates, admits of easy treatment. We shall only have occasion to require the solution for the steady state acquired by the dielectric after a difference of potential between the plates has been established and kept constant. Let the potential of one plate be V, and that of the other zero. Then, if τ denote the specific resistance and K the specific inductive capacity at a point whose distance from the first plate is x, we have

$$\frac{d}{dx}\left(\frac{1}{\tau}\frac{dV}{dx}\right)=0, \quad \text{and} \quad \frac{d}{dx}\left(K\frac{dV}{dx}\right)=-4\pi\rho,$$

where ρ is the volume density of electricity. Hence $-\frac{1}{\tau}\frac{dV}{dx}$, which is equal to the current c per unit area, is constant, and therefore

$$c\frac{d}{dx}(K\tau)=4\pi\rho.$$

Hence, by integration, the whole quantity of electricity stored in the dielectric is

$$\frac{Ac}{4\pi}(K_0\tau_0-K_1\tau_1);$$

A being the area of one of the plates. Here K_1 and K_0 are the specific inductive capacities, and τ_1 and τ_0 the specific resistances, at the surfaces of the dielectric. Hence the amount of electricity stored, or the amount of what is known as the residual charge, or the residual discharge, depends, at any rate in the case under consideration, on the state of the surfaces only, and not on the manner of variation of the specific inductive capacity and specific resistance in the interior of the dielectric, except in so far as these affect the value of the current c. Furthermore, as the residual charge is always of the same sign as the primary charge, it follows that $K_0\tau_0$ is always greater than $K_1\tau_1$ when a positive current goes from the first plate to the second, that is, when V is positive. When V is negative $K_0\tau_0$ is always less than $K_1\tau_1$. It is clear, therefore, that the surface values of one or both of the quantities K and τ depend on the field of force. The charge Q_1 on the first plate is $\frac{Ac}{4\pi}K_1\tau_1$, and the charge Q_0 on the second plate $-\frac{Ac}{4\pi}K_0\tau_0$, the sum of the charges on the plates and the charge in the dielectric being, of course, zero. It will be noted that there can be no residual charge if $K_0\tau_0=K_1\tau_1$, or if $c=0$. If q denote the charge in the dielectric, we have

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[*] Communicated by the Authors.

$$\frac{q}{Q_1}=\frac{K_0\tau_0-K_1\tau_1}{K_1\tau_1},$$

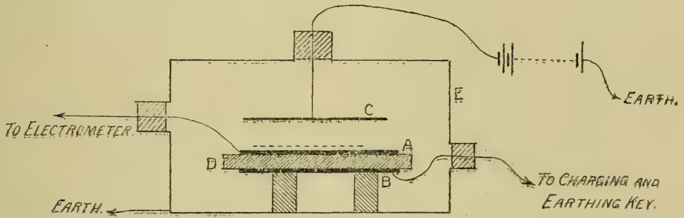
or assuming $K_0=K_1$, which would seem not to be devoid of probability in an apparently homogeneous dielectric,

$$\frac{q}{Q_1}=\frac{\tau_0-\tau_1}{\tau_1}.$$

If this be so, we must explain the existence of q by a difference between τ_0 and τ_1, and τ_0 must be greater than τ_1. That is to say, the resistance of the dielectric at the cathode must be greater than it is at the anode, and this difference must be produced by the field of force. An explanation is supplied by the electron theory according to which the specific resistance of a conductor is given by the expression $\frac{4\alpha\theta}{nule^2}$. Probably the only quantities in this expression which can be different for the two surfaces of the dielectric are n and l, n being the number of free electrons per unit volume and l their mean free path. It is easy to understand that the number of free electrons per unit volume close to the anode will be greater than that close to the cathode, just as the density of the atmosphere decreases with an increase of height. It is possible that l, the mean free path, may be less at the anode than at the cathode, owing to the increase in the value of n, but if it be remembered that the motion of a free electron takes place among both fixed atoms and free electrons, it will be seen that the change in the value of l is probably very small. We have, therefore, $\frac{\tau_0-\tau_1}{\tau_1}=\frac{n_1-n_0}{n_0}$, n_1 being the number of free electrons per unit volume at the anode, and n_0 the corresponding number at the cathode. According to this view, the residual charge is due to changes of the surface resistances consequent on a displacement of the free electrons under the action of the field of force, and $\frac{q}{Q_1}=\frac{n_1-n_0}{n_0}$. When the field is removed by connecting the two metal plates the residual charge disappears gradually, and, after a time, n_1 becomes equal to n_0.

It is not necessary, then, for a residual charge, that the dielectric should be heterogeneous, unless the rearrangement of the free electrons caused by electric force be regarded as constituting heterogeneity. In this connexion it may be worth while quoting a remark of Maxwell ('Electricity and Magnetism,' vol. i. 3rd edition, p. 457). "It by no means follows," he says, "that every substance which exhibits the phenomenon is so composed, for it may indicate a new kind of electric polarization of which a homogeneous substance may be capable, and this in some cases may perhaps resemble electrochemical polarization much more than dielectric polarization."

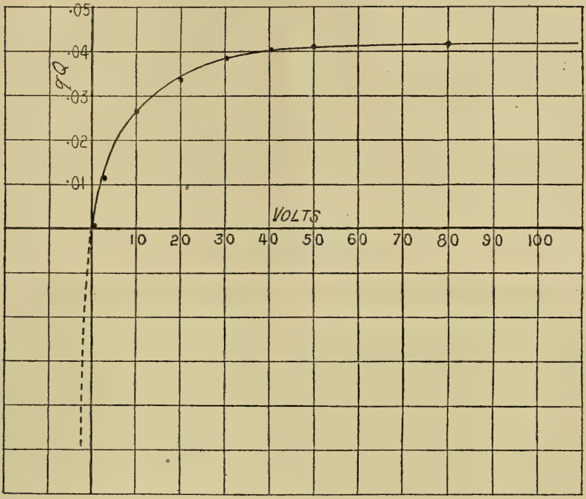
Fig. 1.



The method of measuring the residual discharge will be understood from fig. 1. The dielectric was a plate D of hard brittle amorphous sulphur of a uniform thickness of ·153 cm. placed between two smooth circular plates of zinc A and B, each having a diameter of 10 cm. Both the surfaces of D were like smooth glass. The plate B was insulated by two blocks of paraffin, and the whole condenser was inside an earthed cylindrical box E. B was connected by a wire passing through a plug of paraffin wax, to a key, by means of which it could be charged to any available potential, or earthed, and A was connected by a wire passing through another plug to the electrometer. Another zinc plate C, connected to a battery of cells, was placed above A, the air between A and C being ionized by means of a small quantity of uranium oxide placed on A. The number of cells in connexion with C was always greater than that required to produce a saturation current in this air space. When a residual charge was to be measured A was at first earthed and B charged up to a definite potential for a definite time. B was then earthed and A insulated immediately afterwards. A special key was constructed to make the interval of time between the earthing of B and the insulating of A as short as possible. The electrometer will now charge up, but will be continuously discharged by the ionized air between C and A, and when the needle comes back to zero, the time which has elapsed from the instant at which A was insulated will be a measure of the residual charge, provided that, when the needle comes back to its resting point, all the charge has disappeared. This can easily be tested by finding whether the rate of motion of the needle after passing the resting point is the same as when no charge had been given to the condenser. It was generally found that a small charge was left when the needle had come back to zero, and for this reason it was always allowed to move through 330 divisions of the scale after having come to zero, and the excess of the time required for these 330 divisions over that required to describe the same interval on the scale when no charge had been given to the condenser, was added to the time to the resting point. The rate of motion of the needle for the last 40 of these 330 divisions was always taken, and if it was found to be less than the rate when the condenser was without charge, a smaller quantity of uranium oxide was used until it was quite certain that all the residual charge had been registered. It will be seen that the method is a very convenient one for measuring either a primary or residual charge, and can be quite readily applied to determine the relation between the amount of residual charge and the time of charging for any given applied electrostatic pressure. Curves showing this relation were obtained for different pressures, and show its known asymptotic character.

The curve shown in fig. 2 gives the ratio q/Q, that is the ratio of the residual charge of the condenser to the primary charge for different values of the applied pressure, the time of charging being always greater than that required to make the residual charge closely approach its asymptotic value. It was thought that, inasmuch as the amount of the residual charge depends on the surface resistance, there might be a difference for plates of different metals, but no such difference could be detected having a greater value than the possible experimental error, which was about one in a hundred. It was also thought that there might be a lower limit to the electrostatic pressure capable of producing a residual charge,

Fig. 2.



but no such limit could be found, and it seems, therefore, that the smallest electric force if applied long enough to the dielectric will produce some displacement of the free electrons. Though the curve in fig. 2 is, no doubt, an exponential curve, it approximates very closely to an equilateral hyperbola, the various readings, of which a few are indicated in the figure, falling into position with surprising accuracy. This fact, in itself, might be an indication that the residual charge is not mainly due to any haphazard space variation of K and τ, but to something quite simple in its nature, and wholly distinct from the ordinary mechanical properties of the dielectric, and to something, too, produced by the impressed electric force.

The curve approximates closely to that whose equation is

$$y(x+10) = {\cdot}05\, x,$$

y being the ratio q/Q, and x the pressure in volts applied to the condenser. Thus we have, roughly,

$$\frac{q}{Q} = \frac{{\cdot}05\mathrm{V}}{\mathrm{V}+10},$$

V being the difference of potential of the two plates in volts.

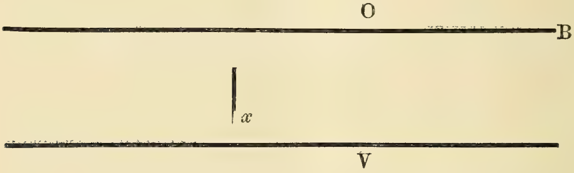
When V is indefinitely increased q/Q tends to the value ·05 or one twentieth. Since

$$\frac{n_1-n_0}{n_1}=\frac{\cdot 05\mathrm{V}}{\mathrm{V}+10},$$

the value of $\frac{n_0}{n_1}$ for high pressures is $\frac{19}{20}$.

The following is a mathematical discussion of the problem which arises in this experiment.

Fig. 3.



Consider a dielectric between two parallel plates A and B at potentials V and O respectively, and let d be the density of the free electrons in the natural state, that is the quantity of negative electricity possessed by unit volume owing to the free electrons which it contains. Then when the field is put on, the density in the neighbourhood of A will be greater than the density in the neighbourhood of B. Let ρ denote the density at any point. In the natural state the force due to the free electrons will be

$$-4\pi d\left(x-\frac{a}{2}\right),$$

where a is the distance between the plates, the specific inductive capacity of the dielectric being taken as unity. But, since the whole force is zero in the natural state, it is clear that the force due to the positive atoms and bound electrons will be

$$4\pi d\left(x-\frac{a}{2}\right).$$

Hence, if X be the impressed force, the force at any point will be

$$\mathrm{X}+2\pi d\,(2x-a)+\text{Force due to the free electrons, as rearranged by the total field.}$$

Denoting the latter force by P, we have the force at any point per unit quantity of positive electricity equal to

$$\mathrm{X}+2\pi d\,(2x-a)+\mathrm{P}.$$

The force P is positive at A, vanishes for a certain value of x, and is negative at B. If

$$\mathrm{X}=0, \quad \mathrm{P}=-2\pi d\,(2x-a).$$

Let p be the pressure due to the free electrons; then, since $p=\mathrm{K}\rho$, we have

$$\frac{\mathrm{K}}{p}\cdot\frac{dp}{dx}=-\mathrm{X}-2\pi d\,(2x-a)-\mathrm{P}$$

and

$$\frac{d\mathrm{P}}{dx}=-4\pi\rho,$$

$$\therefore \quad \mathrm{K}\frac{d}{dx}\left(\frac{1}{p}\frac{dp}{dx}\right)=4\pi\,(\rho-d).$$

Let $n=$ number of free electrons per unit volume at any point, and N the number of free electrons per unit volume in the natural state. Then $d=\mathrm{N}e$, and $\rho=ne$, e being the charge of an electron. We have then

$$\mathrm{K}\frac{d}{dx}\left(\frac{1}{n}\frac{dn}{dx}\right)=4\pi e\,(n-\mathrm{N}),$$

or

$$\frac{d}{dx}\left(\frac{1}{n}\frac{dn}{dx}\right)=\lambda(n-\mathrm{N}),$$

where

$$\lambda \text{ is written for } \frac{4\pi e}{\mathrm{K}}.$$

This differential equation being independent of X will be true for any uniform field applied to the dielectric, and in the particular case we must have

$$\frac{\mathrm{K}}{n}\frac{dn}{dx}=-\mathrm{X}-2\pi\mathrm{N}e\,(2x-a)-\mathrm{P},$$

where

$$\frac{d\mathrm{P}}{dx}=-4\pi ne.$$

Writing

$$2v=\left(\frac{dn}{dx}\right)^2,$$

the above differential equation becomes

$$\frac{d}{dn}\left(\frac{v}{n^2}\right)=\lambda\left(1-\frac{\mathrm{N}}{n}\right),$$

$$\therefore \quad v=\lambda n^2 (n-\mathrm{N}\log n+\mathrm{A}),$$

or

$$\left(\frac{dn}{dx}\right)^2=2\lambda n^2 (n-\mathrm{N}\log n+\mathrm{A}),$$

where A is a constant. Since this equation is true for every uniform field of force, we must have

$$\mathrm{A}=\mathrm{N}\log\mathrm{N}-\mathrm{N},$$

and, therefore,

$$\left(\frac{dn}{dx}\right)^2=2\lambda n^2\left(n-\mathrm{N}-\mathrm{N}\log\frac{n}{\mathrm{N}}\right),$$

$$\therefore \quad \frac{dn}{dx}=-n\left[2\lambda\left(n-\mathrm{N}-\mathrm{N}\log\frac{n}{\mathrm{N}}\right)\right]^{\frac{1}{2}},$$

it being clearly negative at every point. P is therefore determined, and is equal to

$$-\mathrm{X}-2\pi\mathrm{N}e\,(2x-a)+4\pi e\left[\frac{2}{\lambda}\left(n-\mathrm{N}-\mathrm{N}\log\frac{n}{\mathrm{N}}\right)\right]^{\frac{1}{2}}.$$

The experiment on the sulphur plate shows that, very probably, n never differs very much from N.

Let $\frac{n}{\mathrm{N}}=1+\beta$, where β is small.

Then

$$\frac{dn}{dx}=-\mathrm{N}(1+\beta)\left[2\lambda\,.\,\frac{\beta^2}{2}\right]^{\frac{1}{2}},$$

or

$$\frac{d\beta}{dx}=-\sqrt{\lambda\mathrm{N}}\,.\,\beta(1+\beta).$$

$$\therefore \quad \frac{\beta}{1+\beta}=\mathrm{C}\,e^{-\sqrt{\lambda\mathrm{N}}\,.\,x}$$

where C is a constant.[1]

Hence

$$n=\frac{\mathrm{N}}{1-\mathrm{C}\,e^{-\sqrt{\lambda\mathrm{N}}\,.\,x}}.$$

The constant C must be determined by experiment. In the experiment above described, when q/Q was ·05, or when the electric force applied was 80 volts per ·153 cm.,

$$\frac{n_1-n_0}{n_1}=\frac{1}{20},$$

from which it follows that

$$C=\frac{1}{20-19\,e^{-\sqrt{\lambda N}\,.\,a}}.$$

Note.—In the above the existence of the variation of conductivity which is necessary in Maxwell's theory of the residual charge is made to depend on the displacement of the free electrons in the dielectric. But it must be pointed out that this displacement, without any bodily charge in the dielectric, would give rise to a residual charge. When the primary discharge takes place, bound charges are left on both plates which are gradually set free, as the displaced electrons return to the state of uniform distribution. The residual charge is therefore, probably, a more complicated phenomenon than that contemplated in Maxwell's theory.

XL. *The Motion of the Needle of a Quadrant Electrometer. By* W. F. G. Swann, *D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield*[*].

VERY small currents are frequently measured by observing the rate of movement of the needle of a quadrant electrometer as the electricity enters one of the quadrants. Such currents are of course often measured by connecting the quadrant to earth through a very high resistance, and noting the steady deflexion which is produced when the electricity passes into the quadrant at the same rate as it leaves through the high resistance. The former method is more sensitive however, and is very convenient in practice, but even though the electricity passes into the quadrant at a uniform rate, the needle does not move with uniform velocity, owing to its inertia. This effect must doubtless have been noticed by many observers, but though, unless suitable precautions are taken, considerable errors may result I have seen no accounts of any systematic precautions of this nature. In view of the present extensive employment of electrometers, the following discussion of the theory and suggestion of a simple method of avoiding the error may be of interest.

If θ is the angle of deflexion of the needle, the equation of motion is

$$K\frac{d^2\theta}{dt^2}+b\frac{d\theta}{dt}+a\theta=F(t), \quad . \quad . \quad . \quad . \quad (1)$$

where the constants have the usual significance, and $F(t)$ is the couple on the needle due to the electricity which has entered the quadrant. $F(t)$ is of course proportional to the potential of the quadrant.

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[*] Communicated by the Author.

There are two cases of common occurrence. In the first case the difference of potential driving the electricity into the quadrant is large compared with the rise of potential of the quadrant during the observations, in which case $F(t)$ is of the form Xt, where X is a constant. The second case to be considered is the one in which the alteration of the current due to the rise of potential of the electrometer is of importance. In this case if V is the potential of the quadrant, $\frac{dV}{dt}$ is of the form $A-hV$, where A and h are constants, so that

$$V=V_1(1-e^{-ht}),$$

V_1 being the final potential which would be attained by the quadrant after an infinite time. Since $F(t)$ is proportional to V, it is of the form $P(1-e^{-ht})$ where P is a constant.

The solution of (1) corresponding to the case where $F(t)$ is of the form Xt is

$$\theta=\frac{X}{a}\left\{t-\frac{\lambda T}{\pi^2+\lambda^2}-B\,e^{-\frac{2\lambda t}{T}}\sin\left(\frac{2\pi}{T}t-\gamma\right)\right\},$$

where λ, the logarithmic decrement, $=bT/4K$, and

$$\frac{2\pi}{T}=\sqrt{\frac{a}{K}-\frac{b^2}{4K^2}}.$$

On introducing the conditions $\theta=0$ when $t=0$, and $\dot{\theta}=0$ when $t=0$, we readily obtain

$$\tan\gamma=\frac{2\pi\lambda}{\pi^2-\lambda^2},\qquad B=\frac{T}{4\pi}.$$

If the needle were allowed to come to rest for various values of the potential of the quadrant, the position it would take up would of course depend upon that potential. We shall speak of the "Ideal Motion" of the needle as the motion it would have if, for each value of the potential of the quadrant, it assumed the same position as in the above statical case. For the ideal motion corresponding to the present case we have $\theta=\frac{Xt}{a}$. We shall call $\theta-\frac{Xt}{a}$ the error. By differentiating the error with respect to t and equating to zero, we find that it is a maximum when

$$\tan\left(\frac{2\pi}{T}t-\gamma\right)=\frac{\pi}{\lambda}.$$

Considering the case of the electrometer with which the author is at present working, for which $t=14{\cdot}2$ seconds and $\lambda=1{\cdot}11$, we find that the error attains its first and subsequent maxima at $0{\cdot}304\,\mathrm{T}$, $1{\cdot}304\,\mathrm{T}$, $2{\cdot}304\,\mathrm{T}, \ldots$ &c. respectively. The error at its first maximum amounts to about 45 per cent., at the second maximum 8 per cent., and indeed, if we measure times and the positions of the needle from the time and position occupied by the needle when the quadrant was released from its earth connexion, even though we allow such a time t_1 to elapse that the exponential term has practically died down to zero, we shall make an error of $\dfrac{100\lambda\mathrm{T}}{t_1(\pi^2+\lambda^2)}$ per cent. Thus suppose, for example, in the case of the instrument here considered the quadrant were released, and an observation were taken 60 seconds later. The exponential term would have died down to a very small amount by this time, but there would still remain an error of 2·4 per cent. In fact, though the needle ultimately moves with uniform velocity, the straight line representing its motion, when produced back, does not pass through the origin, a certain amount of time having been as it were lost in creating motion in the needle. As observations are frequently measured from the instant of releasing the quadrant, the error here discussed is worthy of serious consideration.

The error may be completely avoided by taking successive observations when the periodic term is zero. All readings measured from the position of rest of the needle will then be wrong, but they will be wrong by a constant amount, so that if the reading corresponding to the position of rest is omitted, the others will serve to determine accurately the ideal motion of the needle. Thus the first reading should be taken at $t=\dfrac{\mathrm{T}}{2\pi}\gamma$, and the succeeding readings at intervals of a period. For example, in the case of the instrument above referred to, the first observation should be taken at $t=1{\cdot}5$ seconds, the second at $t=15{\cdot}7$, and so on.

If the period of the needle is not an exact number of half seconds, the method may appear rather troublesome, if one is using a chronometer beating half seconds, but in practice no difficulty occurs, for it is sufficient for the purpose in hand to take the period as corresponding to the nearest whole number of half seconds. Although the error thereby introduced into the periodic term is cumulative in the successive observations, the whole term itself soon dies out owing to the exponential factor.

Case where $F(t)$ *is of the form* $P(1-e^{-ht})$ *.—The solution of (1) corresponding to this case is

$$\theta = \frac{P}{a}\left\{1 - \left(\frac{a}{Kh^2 - bh + a}\right)e^{-ht} - c\,e^{-\frac{2\lambda t}{T}}\sin\left(\frac{2\pi}{T}t - \delta\right)\right\}. \quad (2)$$

The conditions $\theta=0$ when $t=0$ and $\dot{\theta}=0$ when $t=0$ give

$$\tan\delta = \frac{\pi(4\lambda - hT)}{2\pi^2 - 2\lambda^2 + h\lambda T}.$$

It is unnecessary for our present purpose to write down the expression for c. The ideal motion of the needle is given by

$$\theta = \theta_1(1 - e^{-ht}), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where θ_1 is written for the maximum deflexion P/a.

Owing to the presence of the term involving e^{-ht}, it is impossible to take the observations in such a way as to give directly a result entirely free from errors due to inertia; we can, however, easily arrange the observations so as to be readily susceptible of correction. If we write $1-k$ for

$$Kh^2/a - b\,h/a + 1,$$

we can write (2) in the form

$$\theta = (1-k)^{-1}\frac{P}{a}\left\{1 - e^{-ht} - k - c(1-k)\,e^{-\frac{2\lambda t}{T}}\sin\left(\frac{2\pi}{T}t - \delta\right)\right\};$$

k may easily be expressed in terms of λ and T in the form

$$k = \frac{4h\lambda T - h^2T^2}{4(\pi^2 + \lambda^2)}.$$

If the first and successive observations are taken when the periodic term is zero, the difference of any pair of these observations will give $(1-k)^{-1}$ times the difference for the corresponding pair in the ideal motion. In order to obtain exactly the same values as for the ideal motion, the first observation should be taken when $t = \frac{T}{2\pi}\delta$, and the succeeding observations at intervals of a period, the observations should all be multiplied by $(1-k)$, and the fraction k of the maximum deflexion P/a should be added.

h may be obtained sufficiently accurately for substitution in these correcting terms, by assuming the observed values of θ to obey the ideal relation (3).

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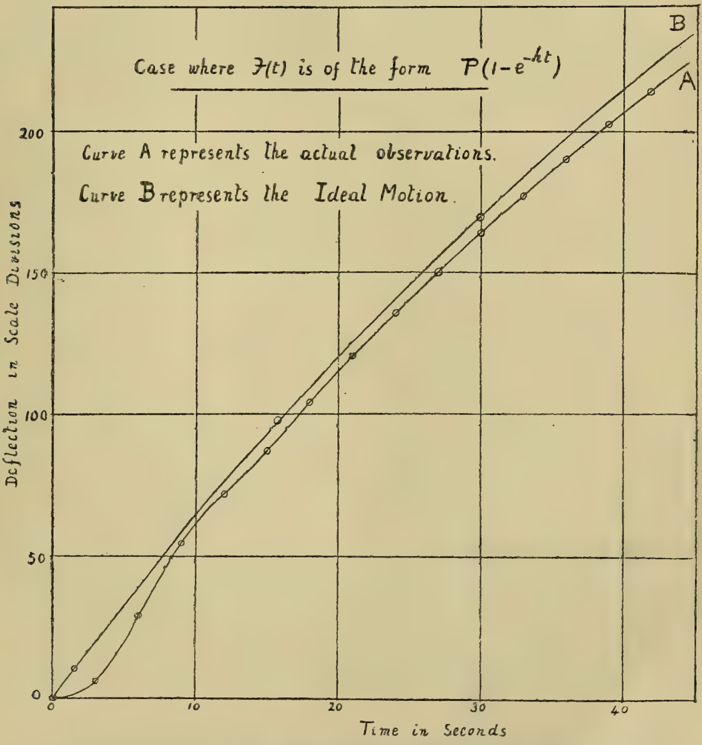
* All the expressions corresponding to the preceding problem may of course be obtained from those of the present problem by putting h equal to infinity, and P equal to zero, subject to the relation $Ph = X$.

The accompanying table (Table I.) and curve A represent the results of an experiment made with the instrument already referred to.

TABLE I.

Time (seconds).	Deflexion.	Time (seconds).	Deflexion.
0	0	24	135·7
3	5·8	27	150·2
6	28·9	30	164·3
9	54·7	33	177·6
12	71·7	36	190·2
15	87·2	39	202·3
18	104·2	42	214·2
21	120·3		



The quadrant was connected through a very high resistance to one pole of a battery consisting of two cadmium cells in series, the other pole being earthed. The quadrant was released from earth, and observations were taken every three seconds, the present table representing the mean results of three experiments. The effect of the periodic term is clearly shown, the first hump being very marked. The first maximum of the periodic term occurs when

$$\tan\left(\frac{2\pi}{T}t-\delta\right)=\frac{\pi}{\lambda},$$

or on substitution of the constants deduced below, at $t=4{\cdot}2$.

The steady deflexion θ_1 corresponding to two cadmium cells was 552·8, so that taking the case where $\theta/\theta_1=0{\cdot}25$ for which $t=24{\cdot}5$, we readily calculate $h=0{\cdot}0117$. Since $T=14{\cdot}2$ and $\lambda=1{\cdot}11$, the correcting factor $(1-k)$ is $1-0{\cdot}0164=0{\cdot}984$, and $\delta=0{\cdot}104(2\pi)$, so that according to our rule for taking the observations, we should take the first at $t=1{\cdot}5$, the second at $t=15{\cdot}7$, and so on. In order to test the theory, let us take the readings corresponding to the above times for the curve A †, multiply by the correcting factor 0·984, and add on the quantity (0·0164)(552·8). We thus obtain the corrected values θ' given in Table II.

TABLE II.

Time t.	Actual reading from curve θ.	Corrected reading θ'.	Calculated value of θ'.
1·5	1·2	10·3	10·1
15·7	90·5	93·1	96·8
29·9	163·5	169·9	169·9*

The values of θ' should satisfy the equation

$$\theta'=552{\cdot}8(1-e^{-ht}),$$

and the third and fourth columns show how near the agreement is. The number marked with an asterisk represents the observations used to calculate h, and B is the theoretical curve drawn to correspond to this value of h. The points marked on the curve B represent the corrected readings given in the third column of the table, and it is obvious that while the corrected readings fit the curve almost perfectly, the uncorrected readings corresponding to curve A differ from the theoretical values by amounts which vary greatly, especially for the first fifteen seconds. The curves A and B diverge in the position corresponding to the time when the observations ended; this is perfectly consistent with the theory, though the curves would of course meet ultimately at $t=\infty$.

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† The scale of the actual curve used was much larger than that of the reduced reproduction here shown.

Physical Laboratory,
The University of Sheffield,
May 29, 1912.

XLI. *Density of Liquids and Refractive Index of Liquids in Contact.* *By* A. L. Clark, *Ph.D., Prof. of Physics, Queen's University, Kingston, Ontario* *.

WHILE experimenting with various pairs of liquids which remain sufficiently insoluble to maintain a meniscus of separation, I came across the phenomenon described below. Chloroform, which is nearly insoluble in water and possesses a density of about 1·4 at ordinary temperature, has a critical density of about ·5. The density of water at 260°, the critical temperature of chloroform, is about ·66, so that as the temperature rises, the density of chloroform falls off more rapidly than that of water, and at one temperature they are equal. I placed chloroform and water together in a Natterer's tube and heated in a paraffin bath. At a few degrees below the critical temperature of chloroform the equilibrium becomes unstable and the system overturns, the chloroform rising to the top. As it cools down again the chloroform sinks again to the bottom †.

The temperature at which the phenomenon occurs is higher than was expected from the study of liquid density curves of other liquids (that for chloroform seems never to have been investigated). This is due no doubt to the solution of chloroform in the water and water in the chloroform tending to equalize the densities. With pure chloroform and water, however, the upset is certain. The phenomenon is very interesting to watch, particularly when the system is cooled. The chloroform settles down into the water stretching the surface film more and more, and finally breaks through.

Another very interesting phenomenon discovered in the same experiment was observed as follows. The meniscus between the two liquids is visible on account of the different indices of refraction. At ordinary temperature the index for chloroform is 1·45, while that of water is 1·33. The index for chloroform decreases more rapidly with rising temperature than does that of water, so that eventually the index of chloroform falls below that of water. When the two indices are equal the separating surface disappears from view to reappear again when the temperature is raised still more. The disappearance is so complete that when the experiment was first made it was given up at this point, as there was every appearance of homogeneity just as though mixture of the two liquids was complete. In the case described above the temperature for disappearance of the meniscus is considerably below that at which the liquids change places.

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* Communicated by the Author.

† The same phenomena may be seen with aniline and water.

The tube used was a thick-walled tube about 6 cm. long with internal diameter of 7 mm.

XLII. *Notices respecting New Books.*

Bibliography of Non-Euclidean Geometry, including the Theory of Parallels, the Foundations of Geometry, and Space of n *Dimensions.* By Duncan M. Y. Sommerville, *M.A.*, *D.Sc.* Printed and published by Harrison & Sons, London, for the University of St. Andrews. 1911.

BY the preparation of this bibliography Dr. Sommerville has earned the gratitude of all students of the branches of mathematics which bear upon the modern developments of non-Euclidean space. Begun as a continuation of Halsted's bibliography of a similar nature, which contains short annotations on the principal works catalogued, the present work finally took a different form; and we have here catalogued the titles of all works from the earliest times to the present which deal with the extended conception of space. Fully half the book is a chronological catalogue, beginning with Aristotle and Plato in the fourth century B.C., and coming down to 1911. In each year the authors' names are arranged alphabetically. There then follow a subject index, with the authors' names and dates given under each heading; an alphabetical index of subjects; and an author index, giving titles and dates, from which by reference to the chronological catalogue every needed information can be at once obtained. The book should be in every mathematician's library.

INDEXED.

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XLIII. *The Origin of β and γ Rays from Radioactive Substances.*

By E. Rutherford, *F.R.S., Professor of Physics in the University of Manchester* [*].

FROM a study of the α radiations from active matter, it has been found that each atom of a substance in disintegrating emits one α particle which is expelled with a definite velocity and with a range in air characteristic of that substance. The only exception is the product thorium C, which emits two distinct groups of α rays, each of definite but different range in air. In this case, the atom appears to break up in two distinct ways.

In many transformations β and γ rays are emitted, and, from analogy with the α ray transformations, it would be expected that one β particle of definite speed would be emitted for the disintegration of each atom. The experiments, however, of v. Baeyer, Hahn and Miss Meitner [†], and later of Danysz [‡], have shown that the emission of β rays from a radioactive substance is in most cases a very complicated phenomenon. The complexity of the radiation is most simply shown by observing the deflexion of a narrow pencil of β rays by a magnetic field in a vacuum. If the rays fall on a photographic plate, a number of sharply marked bands are observed, indicating that the rays are complex and consist of a number of homogeneous groups of rays, each of which is characterized by a definite velocity.

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[*] Communicated by the Author. A preliminary paper on this subject was read before the Manchester Literary and Philosophical Society, 1912.

[†] v. Baeyer and Hahn, *Phys. Zeit.* xi. p. 488 (1910); v. Baeyer, Hahn and Meitner, *Phys. Zeit.* xii. pp. 273, 378 (1911); xiii. p. 264 (1912).

[‡] Danysz, *C. R.* cliii. pp. 339, 1066 (1911); *Le Radium*, ix. p. 1 (1912).

This complexity of the radiation is best shown by those products which emit penetrating β rays and intense γ rays; for example, each of the products thorium D and mesothorium 2 emits a number of well defined groups of β rays and penetrating γ rays. The complexity of the β rays is, however, most markedly exhibited in the case of the products radium B and radium C, when a very strong source of radiation is employed. Using as a β ray source a thin-walled glass tube containing a large quantity of radium emanation, Danysz found that radium B and radium C together emitted about 30 groups of homogeneous rays.

Notwithstanding this great complexity of the β rays from these products, general experiment has shown that the number of β particles emitted by them is about that to be expected if each atom in breaking up emitted only one β particle. This important point has been carefully examined by H. Moseley[*], who has shown that not more than 2·13 β particles are emitted during the disintegration of one atom of radium B and one atom of radium C. By separating these two products, Moseley found that the atom of each product contributes about half of this number. It thus seems clear that on an average one atom in disintegrating emits about one β particle.

In addition to the well-known β ray products, Baeyer, Hahn and Meitner have shown by the photographic method that radium itself and radium D emit a weak β radiation which consists in each case of two definite groups of β rays. In these cases, no evidence of the emission of a γ radiation has yet been observed.

There appears to be no doubt that the γ rays from active matter are closely connected with the β rays, and that both types of rays arise in the transformation of the same atom. Investigation, however, has shown that there is not any obvious relation between the relative intensity of the β and γ rays which are emitted from a given product. The products radium C, thorium D, and mesothorium 2 emit β and γ rays of about the same penetrating power and in about the same relative proportion. On the other hand, uranium X, which emits penetrating β rays, gives relatively few γ rays. A still more striking instance is the β ray product radium E, which, as Gray[*] has shown, emits relatively an exceedingly weak γ radiation. It may prove significant that only those products which emit well-defined groups of β rays emit also a strong γ radiation; for, as far as observation has gone, the β rays from uranium X and radium E give a continuous spectrum in a magnetic field.

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[*] Moseley, "The number of β particles emitted in the transformation of radium." Read Roy. Soc. June 13, 1912.

In order to account for the emission of groups of homogeneous rays from a single product, it is necessary to suppose either that the atom breaks up in a number of distinct ways, each of which is characterized by the emission of β particles of definite velocity, or that the β rays are altered in velocity in some definite way during their escape from the disintegrating atom. On the first hypothesis, it might be anticipated that the different modes of transformation of a β ray product would give rise to a series of new products, but only one is observed. In addition, the energy emitted during the transformation from one type of matter into another would vary widely for different atoms of the same substance, and this seems improbable. On the second hypothesis, it is supposed that the disintegration of each atom takes place in exactly the same way with the emission of the same amount of energy, but that the energy of the β particle may be decreased by definite but different amounts due to transformations of its energy in its passage through the atomic system from which it originates. Since it is known that β rays in escaping from an atom give rise to γ rays, it is natural to suppose that the loss of energy of the β particle in escaping from the atomic system is connected in some way with the excitation of γ rays.

The work of Barkla and others on the X rays have brought out clearly that under suitable conditions of excitation, each element emits one or more definite types of X radiation which are characteristic of the element. Barkla[†] has determined the coefficient of absorption μ in aluminium of the characteristic X rays for elements up to atomic weight 140. The value of μ/D for aluminium, where D is the density, decreases rapidly with the atomic weight and varies between 435 for calcium of atomic weight 40·1 to 0·6 for cerium of atomic weight 140·25. Plotting the logarithms of the values of μ/D against the logarithm of the corresponding atomic weights, the points for the heavier elements are found to lie nearly on a straight line. If this straight line be produced, it can be shown by extrapolation that an element of atomic weight 214 should emit a characteristic radiation whose value of $\mu/\mathrm{D}=\cdot 04$ about for aluminium. This is in good accord with the value $\mu/\mathrm{D}=\cdot 0406$ for aluminium found by Soddy and Russell for the penetrating γ rays from radium C. It would thus appear probable that the penetrating γ radiation from radium C is to be regarded as the characteristic radiation of that element excited by the escape of β particles from the atomic system.

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[*] Gray, Proc. Roy. Soc. A. lxxxv. p. 131 (1911); lxxxvi. p. 513 (1912).

[†] Barkla, Phil. Mag. xxii. p. 396 (1911).

Whiddington [*] has shown that the β or cathode particle incident on matter must have a definite minimum speed for each element before the characteristic radiation of the latter is excited. Over the range examined, this velocity is directly equal to $\mathrm{A}\times 10^8$ cm. per second, where A is the atomic weight of the element. If it be supposed that this law holds generally for all the elements, the velocity of the β particle required to excite the characteristic radiation of radium C of atomic weight 214 should be 0·71 of the velocity of light. It is not improbable, however, that the energy $\frac{1}{2}mu^2$ rather than the velocity u is the determining factor for high-speed β particles. Taking this into consideration, the velocity required to excite the characteristic radiation is given by $u=10^8\,\mathrm{A}\sqrt{m_0/m}$, where m_0 is the mass of the β particle for slow speeds. On this hypothesis, $u=\cdot 63$ of the velocity of light. The mean value for the two methods of calculation gives $u=\cdot 67$. The corresponding energy of the β particle for the mean value of u is $1\cdot 5\times 10^{13}\,e$ ergs, where e is the charge carried by the β particle. If it be supposed that the whole energy of the β particle is converted into γ radiation, the energy absorbed in exciting the characteristic γ ray should be $1\cdot 5\times 10^{13}\,e$ ergs.

If the complexity of the β radiation is connected with the emission of γ rays, it is to be expected that some definite relation should exist between the energies of the β particles in each of the groups emitted. From this point of view, it is of interest to examine whether there is any evidence of such a relation for the β rays emitted by radium B and C. The results given by Danysz are included in the table on the opposite page.

The various groups differ widely in photographic intensity. This is designated in column 1 by the symbols s = strong, m = mean, f = feeble, vf = very feeble. Each group is defined by a number given in the second column; for the sake of completeness, two groups of rays of low velocity A and B

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[*] Whiddington, Proc. Roy. Soc. A. lxxxv. p. 323 (1911).

Intensity.	No.	Hρ.	β.	Energy.	Intensity.	No.	Hρ.	β.	Energy.
	A	Hahn	·36	$0·353 \times 10^{13}$ *e.*	f	11	2190	·790	$2·595 \times 10^{13}$ *e.*
	B		·41	0·468 ,,	s	12	2870	·862	3·711 ,,
s	1	1320	·615	1·218 ,,	f	13	3140	·882	4·155 ,,
f	2	1390	·634	1·322 ,,	f	14	3420	·897	4·60 ,,
vf	3	1490	·660	1·475 ,,	f	15	4000	·920	5·52 ,,
s	4	1580	·682	1·616 ,,	s	16	4670	·940	6·585 ,,
f	5	1680	·703	1·771 ,,	f	17	4800	·943	6·79 ,,
vf	6	1750	·718	1·885 ,,	f	18	4980	·946	7·07 ,,
s	7	1830	·735	2·017 ,,	m	19	5100	·949	7·26 ,,
m	8	1900	·748	2·132 ,,	s	20	5700	·957	8·18 ,,
f	9	1970	·760	2·246 ,,	f	21	5990	·962	8·63 ,,
s	10	2150	·786	2·535 ,,	complex	22	11200	·988	16·6 ,,
					complex	23	18100	·996	27·0 ,,

observed by Hahn are added to those given by Danysz. The third column gives the value of Hρ experimentally observed; the fourth column β the ratio of the velocity of the β particle to the velocity of light, calculated from the Lorentz-Einstein formula. In the fifth column I have added the value of the energy of the β particle. The value of e/m for the β particle is taken as $1·772 \times 10^7$ e.m. units.

Starting from group No. 21, the differences between the energies of the individual β particles comprising the different groups are shown in column 2 of the following table:—

Number of group.	Observed difference in energy.	$p\mathrm{E}_1 + q\mathrm{E}_2$.	Calculated difference in energy.
(21)−(20)	$·45 \times 10^{13}$ *e.*	E_1	$·456 \times 10^{13}$ *e.*
,, −(19)	1·37 ,,	$3\mathrm{E}_1$	1·37 ,,
,, −(18)	1·56 ,,	E_2	1·56 ,,
,, −(17)	1·84 ,,	$4\mathrm{E}_1$	1·82 ,,
,, −(16)	2·05 ,,	$\mathrm{E}_1+\mathrm{E}_2$	2·01 ,,
,, −(15)	3·11 ,,	$2\mathrm{E}_2$	3·11 ,,
,, −(14)	4·03 ,,	$2\mathrm{E}_1+2\mathrm{E}_2$	4·02 ,,
,, −(13)	4·48 ,,	$3\mathrm{E}_1+2\mathrm{E}_2$	4·48 ,,
,, −(12)	4·92 ,,	$4\mathrm{E}_1+2\mathrm{E}_2$	4·94 ,,
,, −(11)	6·03 ,,	$3\mathrm{E}_1+3\mathrm{E}_2$	6·03 ,,

On examining these differences, it is seen that they can be expressed closely by the relation $p\mathrm{E}_1 + q\mathrm{E}_2$, where $\mathrm{E}_1 = 0·456 \times 10^{13}\,e$, $\mathrm{E}_2 = 1·556 \times 10^{13}\,e$, and p and q are whole numbers which may have any values 0, 1, 2, 3, &c. The differences calculated on this hypothesis are shown in the last column, and are observed to be in close agreement for the whole series of lines from No. 21 to No. 11. This relation does not hold below line No. 11, but in all probability most of the lines, Nos. 1 to 10, belong to radium B and not to radium C. The energy of the β particle for group No. 21 is $8{\cdot}63 \times 10^{13} e$, while its velocity is ·962 of the velocity of light. Groups 22 and 23 are not included in the calculation, for Danysz states that No. 22 includes from 3 to 5 groups of β rays, of which only the average velocity is given; similarly No. 23 is considered to be a complex group.

The values of the velocity of the β particles will require to be known with great accuracy before such a relation as is indicated can be definitely established; but it does not appear likely that the connexion observed is accidental. It is of interest to note that the value of $E_2 = 1{\cdot}556 \times 10^{13} e$ is in fair accord with the calculated energy of the β particle, viz., $1{\cdot}5 \times 10^{13} e$, which would be required to excite the characteristic radiation from radium C. The value of E_1 may in a similar way be connected with the energy required to excite the second type of characteristic X radiation which has been observed in a number of elements by Barkla.

It is possible that some of the groups from Nos. 10 to 1 may also belong to radium C. For example, No. 8 fits in well with a difference $4E_1 + 3E_2$ from No. 21. Hahn has determined the velocity of the stronger groups of rays from radium B and radium C separately. For radium B, the values $\beta = {\cdot}36, {\cdot}41, {\cdot}63, {\cdot}69, {\cdot}74$ are given. The last three no doubt correspond to groups Nos. 1, 4, and 7 respectively given by Danysz. A group for which $\beta = {\cdot}80$, which appears to correspond to No. 10, is ascribed to radium C. Group No. 10, however, does not fit in at all with the relation found between Nos. 11 to 21. It would be of great value to determine definitely the division of the groups of β rays observed between radium B and radium C.

If the groups Nos. 10 to 1 supposed to belong to radium B be analysed in a similar way to the groups for radium C, the differences may be approximately expressed by the relation $pE_1 + qE_2$ where $E_1 = {\cdot}114 \times 10^{13} e$ and $E_2 = {\cdot}144 \times 10^{13} e$. The agreement, however, between calculation and theory is not nearly so good as for the case previously considered, and it is doubtful whether any weight can be attached to it. For the slow velocity β rays here considered, the reduction of velocity in passing through the glass walls of the emanation tube is quite appreciable, and the correction is different for each group. Until this correction is made, it does not seem possible to draw any definite conclusions.

The simplest way of regarding this relation between the groups of β rays is to suppose that the same total energy is emitted during the disintegration of each atom, but that the energy is divided between β and γ rays in varying proportions for different atoms. For some atoms most, if not all, of the energy is emitted in the form of a high-speed β particle; in others the energy of the β particle is reduced by definite but different amounts by the conversion of part of its energy into γ rays. Suppose, for example, the total energy liberated in the form of β and γ rays during the transformation of one atom is E_0. If the β particle before it escapes from the atom passes through two regions where the energy required to excite a γ ray is E_1 and E_2 respectively, the resulting energy of the β particle is $E_0-(pE_1+qE_2)$, where p and q are whole numbers corresponding to the number of γ rays excited in each region. The energy emitted in the form of γ rays is pE_1+qE_2, and p γ rays of energy E_1 and q of energy E_2 appear.

According to this view, the transformation of one atom gives rise to only one β ray, but to p γ rays of one kind and q of another. The groups of homogeneous β rays observed are the statistical effect due to a large number of disintegrating atoms. The relative distribution of β particles amongst the numerous groups of homogeneous rays will depend on the probability that 0, 1, 2, &c. of the units of energy E_1 and E_2 are abstracted from the β particle in traversing the atom.

This mode of regarding the connexion between β and γ rays suggests that the number of γ rays emitted from radium C is considerably greater than the number of β rays. Assuming that each γ ray from radium C was converted into one β ray, Moseley (*loc. cit.*) found that at least two γ rays appeared for the transformation of one atom of radium C. There is reason to believe that this is a minimum estimate, and that the actual number is two or three times greater.

From the results already considered, it does not necessarily follow that group No. 21 is to be regarded as the head of the β ray series. Evidence on this point can be obtained by calculating the energy E_0 liberated per atom in the form of β and γ rays during the transformation of radium C. In same recent experiments the results of which have been communicated to the Vienna Academy, the writer and Mr. H. Robinson conclude that the heating effect of the β and γ rays from 1 gram of radium is 10·8 gram calories, of which about 4·3 is due to the β rays and 6·5 to the γ rays. An uncertain part of this energy arises from the β and γ rays emitted by radium B; but there will not be much error if it be supposed that the energy of the β and γ rays from radium C in one gram of radium is about 8 gram calories per hour. Supposing, as Moseley found, that one β ray is on the average expelled from each atom of radium C, the energy emitted per atom of radium C in the form of β and γ rays is $17{\cdot}8 \times 10^{13} e$ ergs, assuming that $3{\cdot}4 \times 10^{10}$ β particles per second are emitted from radium C in equilibrium with one gram of radium. This approximately corresponds with the average energy of the β particle included in group No. 22, viz. $16{\cdot}6 \times 10^{13} e$.

Danysz states that No. 22 consists of 3 to 5 groups of β rays, for which only the average velocity of the group is given. In the absence of any definite information of the velocity of the components, it is impossible to ascertain whether any relationship exists between this complex group and the rest of the radium C series. The wide difference between the energies of the β rays included under No. 21 and No. 22 indicates that possibly a third region exists within the atom for which the energy required to excite γ rays is much greater than that for the other two regions considered.

Unless the energy of the β and γ rays from radium determined by experiment has been much underestimated, it does not seem possible to suppose that the swiftest β ray given by Danysz, which has the energy $27 \times 10^{13} e$, can be the head of the β ray series. The existence of such a swift group of β rays is, however, open to some doubt, as Danysz expressly states in his paper. The photographic effect of such swift β rays is very difficult to detect in the presence of a strong photographic action due to the γ rays.

We have so far confined our discussion to the connexion between the β and γ rays emitted from radium C, for in this case the necessary data are far more definite and complete than for any other product. It seems probable, however, that the same general explanation will apply to the emission of β and γ rays from mesothorium 2 and thorium D, both of which emit a number of groups of homogeneous β rays and also penetrating γ rays. In each of these products, the energy emitted in the form of γ rays is of about the same order of magnitude as the energy emitted in the form of β rays.

A difficulty arises in connexion with the β ray products like radium E and uranium X, which emit penetrating β rays but relatively weak γ rays. In the case of uranium X, some penetrating γ rays are observed, but they are weak in relative intensity compared with the γ rays from radium C. It is possible that the atomic structure of uranium X is such that only an occasional β particle loses energy by conversion into γ rays in its escape from the atom. In the case of radium E where the γ rays are very weak in intensity and of slight penetrating power, it seems probable that the β rays originate near the surface of the atom, and consequently do not traverse the regions where penetrating γ rays can be set up. There still remains the difficulty, however, of accounting for the heterogeneity of the β rays which are emitted, to which attention has been drawn by Gray and by Gray and Wilson.

There is one point of interest which has so far not been considered. Bragg has given strong evidence for believing that a β and a γ ray are mutually convertible forms of energy. The energy of a γ ray incident on matter is transformed into the energy of a β ray, and *vice versa.* On this view, it has generally been supposed that the whole of the energy of one γ ray is converted into the energy of one β ray, so that the γ ray disappears and the β particle takes its place. From the point of view outlined in this paper, it is supposed that the β ray originating in the transformation of an atom loses only part of its energy which is abstracted from it in definite units, depending on the region of the atom through which the β particle passes. A swift β ray may consequently give rise to several γ rays in escaping from the atom and yet retain a part of its initial energy.

In a previous paper[*] I have given reasons for believing that the atom consists of a positively charged nucleus of very small dimensions, surrounded by a distribution of electrons in rapid motion, possibly of rings of electrons rotating in one plane. The instability of the atom which leads to its disintegration may be conveniently considered to be due to two causes, although these are not mutually independent, viz., the instability of the central nucleus and the instability of the electronic distribution. The former type of instability leads to the expulsion of an α particle, the latter to the appearance of β and γ rays. The instability which leads to the expulsion of a β ray may be mainly confined to one of the rings of concentric electrons, and leads to the escape of a β particle from this ring with great velocity. The β particle in escaping from the atom passes through the electronic distribution external to it, and in traversing each ring may lose part of its energy in exciting one or more γ rays which have a definite energy, which is characteristic for each ring.

At present we have no definite information of the mode in which the transformation of a β into a γ ray or a γ ray into a β ray takes place, but it is no doubt connected with the structure of the ring of electrons, and possibly with its period of free vibration. The general evidence indicates strongly that the transformation of energy from the γ ray form to the β ray form or *vice versa* takes place in definite units which are characteristic for a given ring of electrons but vary from one to the other. The transformation of energy of the β ray form into the γ ray form appears to take place far more efficiently during the disintegration of an atom than when β rays fall on the atoms of ordinary matter. This is not unexpected, for the conditions in the former case are eminently favourable to the conversion, since the β particle passes directly through the electronic distribution of the atom. It is at the same time to be expected that some of the energy of the γ rays which are formed within the atom should also be converted, in part at least, into β rays again, and should thus give rise to one or more groups of homogeneous rays. It is possible that two groups of slow velocity β rays which appear during the transformation of radium itself may arise in consequence of such a transformation of the γ rays set up by the escape of the α particles from the atom. J. Chadwick, working in the laboratory of the writer, has recently obtained evidence that α rays are able to excite γ rays in falling on ordinary matter.

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[*] Rutherford, Phil. Mag. xxi. p. 669 (1911).

If this be the case, it is to be expected that all α ray products should emit some β rays and γ rays, though probably of very weak intensity in both cases. The excitation of γ rays by α rays is not improbable if the energy of the charged particle rather than its velocity is the determining factor; for although the velocity of the α particle is small compared with that of the ordinary β particle, its energy of motion is much greater.

University of Manchester.
Aug. 16, 1912.

XLIV. *On the Emission of Electrons by Metals under the Influence of Alpha Rays.* *By* H. A. Bumstead *and* A. G. McGougan, *Yale University**.

Introduction.

IN a previous paper under the same title by one of the present authors †, an account was given of some experiments upon the so-called δ-rays which are emitted by metals when struck by α-rays. The emission is known to consist of electrons moving with comparatively small velocities. Maximum estimates of their velocity, based upon the potential difference necessary to cause saturation of the current carried through a high vacuum by these electrons, give about $3 \times 10^8 \frac{\text{cm.}}{\text{sec.}}$, corresponding to a potential difference of about 25 volts; minimum estimates, obtained by measuring the positive potential which a source of δ-rays will attain if insulated in a high vacuum, give velocities corresponding to 1 to 3 volts. Campbell [*] has recently brought forward some evidence for believing that the electrons have considerably smaller velocities even than this, if indeed they have any measurable velocity at all. The experiments to be described in § 3 of this paper, however, render this conclusion improbable.

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* Communicated by the Authors.

† Amer. Journ. Sci. xxxii. p. 403 (1911); Phil. Mag. xxii. p. 907 (1911).

In the previous paper it was shown that there was a close analogy between the emission of δ-electrons by a metal and the ionization of a gas by α-rays. The number of electrons emitted by the metal varies with the speed of the α-particles in the same manner as the number of ions produced in a gas; so that, by interposing various thicknesses of aluminium foil between the source of α-rays and the metal, one can plot a curve entirely similar to the ionization curves first obtained by Bragg. The number of electrons emitted by the metal increases with the number of foils interposed until their combined thickness is nearly equal to the range of the α-rays in aluminium, after which the emission of electrons falls off rapidly. The increase in the number of electrons with diminishing speed of the α-rays, however, is not so great as the increase in the number of ions in a gas [†]. The ionization curve of the metal lies within, or to the left of, the corresponding curve for gaseous ionization and has a less pronounced maximum or "knee" just before the end of the range is reached. This result was anticipated before the experiments were undertaken, for reasons given in the previous paper. The same arguments which led to this conclusion also gave reason to believe that the curve for a metal of high atomic weight, such as gold, would lie within that of a metal of lower atomic weight such as aluminium, just as the latter would lie within the curve of gaseous ionization. This expectation, however, was not fulfilled by the results of the experiments. The curves for gold and for aluminium coincided within the limits of accuracy of the somewhat rough method which was used for determining them.

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[*] Phil. Mag. xxiii. p. 481 (1912).

[†] The increase in the emission as the speed of the α-particles decreases has also been observed by Campbell, Phil. Mag. xxi. p. 276 (1911).

Quite apart from the theoretical reasons discussed in the former paper, it was somewhat surprising to find that two metals which differ so much as aluminium and gold gave, nevertheless, the same ionization curves. For the ionization curves of gases and vapours differ considerably among themselves, not only in the area enclosed (total ionization) but also in their shape[*]. The close similarity between the curves for aluminium and gold gave rise to the suspicion that the electrons which had been producing the effects observed came not from the metals, but perhaps from a layer of adsorbed gas which was the same in both cases. In order to test this possibility the following experiment was made.

§ 1. *Attempt to remove Adsorbed Gases by Heating.*

A strip of thin platinum foil, 6 cm. long, 3·7 cm. wide, and $2{\cdot}4 \times 10^{-4}$ cm. thick, was stretched horizontally between two heavy brass clamps; the clamps were carried each on a vertical copper rod which passed through the cover-plate of the evacuated chamber in which the δ-ray effects took place; the rods were insulated from the plate by ebonite, an earthed guard-tube, and amber, and the joints made tight with sealing-wax. The platinum foil was arranged so that it could be exposed to a pencil of α-rays from polonium deposited on the end of a copper plug 4 mm. in diameter. Between the polonium and the platinum, one could interpose aluminium foils, without interfering with the vacuum, in the manner described in the former paper. Two, three, four, five, or six layers of foil could be interposed, each $3{\cdot}2 \times 10^{-4}$ cm. thick. The case was exhausted to about ·0001 mm. with the help of charcoal and liquid air; one of the insulated copper rods which carried the platinum foil was connected with a quadrant electrometer, the case surrounding the exhausted chamber was charged positively, and measurements of the negative current leaving the platinum were taken in the usual manner. After an "ionization curve" had been determined in this way, the platinum strip could be heated by a current sent through it and the two copper rods, and the curve could be again determined when the liberated gas had been removed.

Even before the platinum strip was heated its behaviour gave evidence that the occluded gases had some effect upon the phenomena, if only a temporary one. With the metals used previously, the saturation value of the current had been obtained with +40 volts on the case. With the platinum, an hour after the liquid air had been applied to the charcoal, it required +160 volts to cause saturation, and the current at this potential was 20 per cent. greater than at 40 volts. Four hours later 120 volts was sufficient to cause saturation, and the current was only 12 per cent. greater than at 40 volts. After an interval of 24 hours, saturation was reached at 80 volts with a 5 per cent. increase over 40 volts. During the same time the magnitude of the current (taken under similar conditions) fell off about 30 per cent. But the *shape* of the ionization curve, obtained by using a saturating potential and interposing aluminium foils, changed very little, if at all, while these very considerable changes were going on in the conditions of saturation and in the actual magnitude of the current. The results are given in Table I. The first line of the table gives the time after the liquid air was applied to the charcoal bulb, the second line gives the value of the currents (with two foils interposed) corresponding to these times; the last five lines of the table give the values of the current when different numbers of foil are interposed, the current with two foils being taken as 100 in each case, to facilitate comparison.

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[*] Taylor, Phil. Mag. xxi. pp. 573, 575 (1911).

Table I.

Time	1 hr.	2 hrs.	4 hrs.	6 hrs.	24 hrs.
C_2	186	174	150	146·5	129
Foils					
2	100	100	100	100	100
3	112·0	111·2	112·3	113·0	111·8
4	103·8	103	105	103·3	104·7
5	59·5	60·3	64	63·7	66·2
6	23·1	23	25·3	25·6	26·6

It will be seen that the relative values for 2, 3, and 4 foils show no progressive change with the time; the differences between them are of the order of magnitude of the experimental errors. The values for 5 and 6 foils, however, appear to increase with the time; these values are on the decreasing portion of the ionization curve, where a small change in the range of the α-rays makes a large difference in the current. The observed increase can be explained by supposing that the progressive removal of occluded gas from the platinum foil slightly diminishes its stopping power for α-rays, and thus the δ-radiation from the emergence side is increased.

After making the measurements which are recorded in the last column of Table I., a current of 12 amperes was passed through the platinum foil. With this current a bright red heat was obtained in the middle of the foil, fading away gradually to the ends which were cooled by conduction through the clamps and copper rods *. The current was continued for 10 minutes, during which time the pressure rose from less than ·0001 mm. to ·004 mm. The charcoal bulb did not absorb the gas, although the liquid air was left on over-night; this is doubtless due to the fact that the gas emitted by the platinum contained considerable hydrogen which is not readily absorbed by the charcoal. The liquid air was then removed, and the Toepler pump was operated, while the charcoal was re-heated to aid in sweeping out the hydrogen. When a pressure of about ·001 mm. had been reached the liquid air was again applied, and the pressure soon fell to less than ·0001 mm. After two hours the value of C_2 was 134, and the variation for the different foils interposed did not differ appreciably from the last column of Table I.

This test, however, was not very satisfactory, on account of the failure of the charcoal to remove promptly the gas emitted by the heated platinum. Accordingly the charcoal bulb was removed and a Gaede pump substituted for the Toepler pump. When a vacuum of ·0001 mm. had been maintained for an hour, measurements were taken as before. Then the strip was heated five times, for ten minutes at a time, with intervals of fifteen minutes between, to avoid too great heating of the clamps and copper rods; the pump was kept running continuously. Measurements of the δ-ray current were then made as before. The results are given in Table II.

TABLE II.

Foils	Before $C_2=150$	After $C_2=134$
2	100	100
3	110	108·2
4	102·7	101·0
5	62·5	61·0
6	24·7	24·2

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* A glass window in the brass case permitted observation of the foil.

Here there does appear to be a slight alteration in the form of the ionization curve, and in the direction expected. But the differences are so slight that no great confidence can be placed in the result. Further experience with the method did not give any reason for hoping that the question as to the effect of adsorbed gases could be definitely settled in this way.

The results of this experiment are susceptible of two quite different interpretations. We may say that, since the heating of the platinum strip did not alter the shape of its ionization curve, we may conclude that this shape is due to the properties of the metal itself and not to adsorbed or occluded gases. On the other hand, we may put the emphasis on the fact that, under certain conditions, at least 30 per cent. of the δ-ray effect is due to such gases, and that when these are removed there is no change in the shape of the curve. If the residual effect is really due to the metal, we must suppose that platinum and the adsorbed gases have ionization curves of very nearly the same shape, which is not altogether probable considering the variations which are met with in the curves of gaseous ionization. From this point of view, therefore, it seems more probable that the δ-ray emission (slow electrons) is mainly due to such a layer of gas, which may be reduced but not entirely removed by the methods which we have employed*.

§ 2. *Determination of the Ionization Curves of Various Metals.*

In the determination of the ionization curve of platinum in the preceding section and of those of gold and aluminium in the previous paper, the metals were so thin that the α-rays passed through them, except when they were near the end of their range. This has the advantage that, at least until the top of the curve is reached, no correction for the charge of the α-rays is necessary, and one need not apply a magnetic field in order to determine this charge. On the other hand, a difficulty results if one wishes to make a careful comparison of different metals. It is impossible to obtain foils of different metals which have the same retarding effect on the α-rays; and hence the *emergence* δ-radiation from the different metals corresponds to different speeds of the α-rays even when the same number of aluminium foils are interposed. This is plainly shown by a comparison of the results for platinum with those for gold and aluminium given in the previous paper. The platinum foil is so much thicker than the others that the entire form of the curve is distorted. Moreover, in the foregoing experiments, very few points on the curve were taken, so that indeed it is only by courtesy that it could be called a curve at all. For these reasons a much more careful determination was undertaken by means of the apparatus shown in fig. 1.

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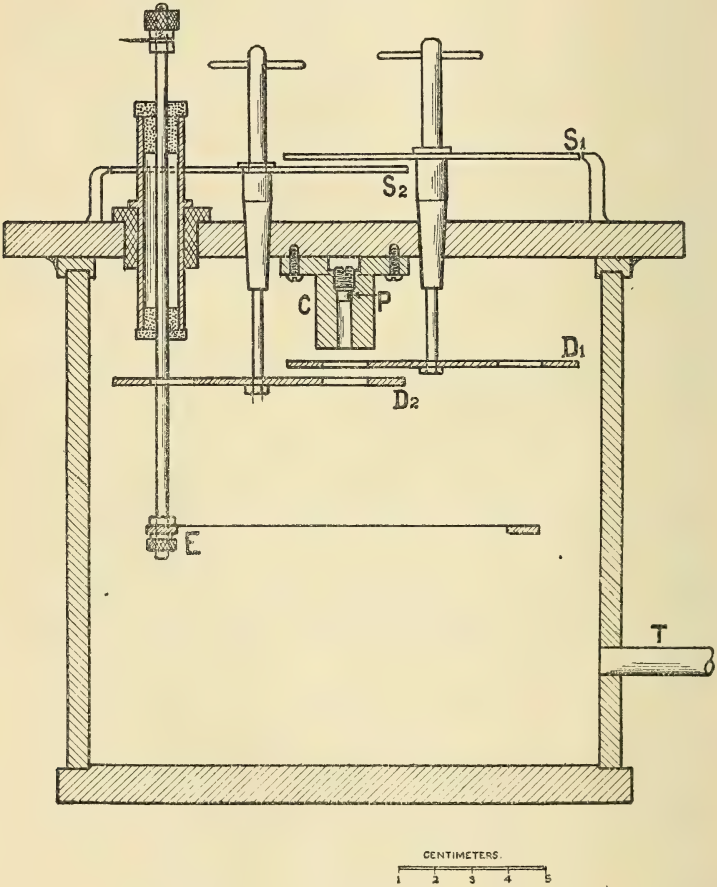
* Since the present investigation was completed a paper has appeared (Pound, Phil. Mag. xxiii. p. 813, May 1912) in which the effect of occluded gases upon the *magnitude* of the δ-radiation is clearly brought out.

Fig. 1.



A copper plug, P, 4 mm. in diameter, whose lower surface is covered with polonium, is surrounded by a brass cylinder, C, which limits the cone of the rays so that they fall completely within the brass ring, E, which supports the sheet of metal under investigation. In order to obtain more points upon the ionization curves, two disks, D_1 and D_2, are used instead of the one which was used in the previous experiments. In order to make the drawing clearer, the rod supporting E is shown in the same plane with the axes of the disks ; in the actual apparatus it is in the plane perpendicular to this. The disks are divided into eight equal sectors. D_1 has a hole 1·5 cm. in diameter cut in each sector. One hole is left open and the others are covered with 1, 2, 3, 4, 5, 6, and 7 layers of aluminium foil of thickness $3{\cdot}2\times10^{-4}$ cm., having a retarding effect upon the α-rays, according to Taylor's results, equivalent to that of 0·58 cm. of air (air equivalent). The disk D_2 has one sector without a hole so that the α-rays can be stopped completely; the other sectors have holes, one of which is left open, others being covered with 1, 2, 3, and 4 layers of thinner aluminium foil, $0{\cdot}64\times10^{-4}$ cm. thick. Thus five of the thin foils are equivalent to one of the thicker. The dials, S_1 and S_2, outside the evacuated chamber enable one to set the disks D_1 and D_2 so that any combination of the thick and thin foils may be interposed in the path of the α-rays, or the brass sector may stop them entirely, or the two holes allow them an uninterrupted passage to the electrode.

The metal plate attached to the ring E was in every case chosen of sufficient thickness to absorb completely the α-rays, so that the δ-electrons were emitted only from the side on which the α-rays were incident. The electrode is insulated from the case by ebonite earthed guard-tube and amber, and is connected to a sensitive gold-leaf electroscope of the Hankel type *. A key is connected to a potentiometer arrangement so that the leaf can be insulated, grounded, or charged to any desired potential ; the volt-sensitiveness was thus taken after each reading. In the following measurements, the sensitiveness was adjusted to give a deflexion of about 25 divisions on the scale of the microscope for 0·2 volt. The tube T is connected to pump, gauge, and charcoal bulb.

When the α-rays fall on the electrode E, they carry over to it their positive charges; the δ-rays which they excite are negatively charged and these, leaving the electrode, add to its positive charge. In order to insure the removal of all the emitted electrons from the electrode, and to prevent the δ-rays emitted by other parts of the apparatus from reaching it, a positive potential of 40 volts is applied to the case. If a sufficient magnetic field is applied, with its lines of force parallel to the electrode, the electrons emitted will be turned

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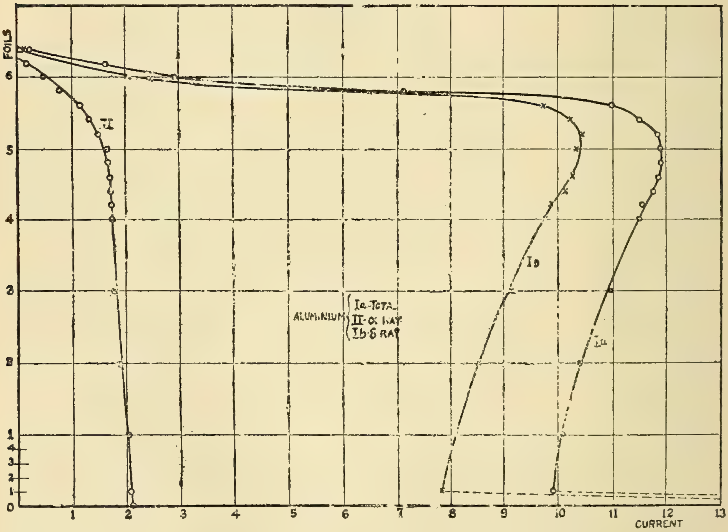
* This instrument is described in the previous paper, Am. Jour. Sci. xxxii. p. 405 (1911); Phil. Mag. xxii. p. 909 (1911).

back to the electrode, and in this way the charge due to the α-rays alone may be determined. For this purpose an electromagnet was constructed of Swedish iron, 2 inches square in section. It was forged into the shape of a rectangle 30 cm. by 25 cm., and a gap left in one side 15·2 cm. long which was just sufficient to embrace the exhausted chamber. It was wound with about 1000 turns of No. 14 cotton insulated, paraffined wire. The field at various points between the poles was measured with a Grassot flux-meter; a current of 3 amperes produced a field, midway between the poles, of 95 gausses. It was found that, with the case earthed, this field reduced the current received by the electrode to a minimum; no further diminution occurred when the current through the magnet-coil was increased to 9 amperes. On account of the large air-gap the field was very nearly proportional to the current.

The results obtained when the electrode was a sheet of aluminium are shown in fig. 2, in which the ordinates represent the number of aluminium foils between the polonium

Fig. 2.



and the electrode, and the abscissæ are the currents measured by the electroscope. Curve I. *a* gives the results with no magnetic field, and thus represents the total effect due to both α- and δ-rays. Curve II. shows the currents observed when the magnetic field was on, due to the charge carried by the α-rays alone. Curve I. *b* is obtained by subtracting the abscissæ of II. from I.a and represents the δ-ray effect, or "ionization" of the metal.

It will be observed from an inspection of Curve II. that the number of α-particles which reach the electrode apparently decreases as more foils are interposed. Up to five thick foils this decrease is approximately linear, and amounts to about 20 per cent. of the total. This is too great a falling off to be attributed to the scattering of the α-rays according to the results obtained by Geiger*. It is possible that an explanation of this effect may be found in the phenomena to be discussed in the following section. Beyond five thick foils, the number of α-particles diminishes rapidly; this is doubtless due to their absorption in the aluminium foils, the more oblique rays being the first to be stopped.

By dividing the abscissæ of I.b by those of II., a curve could be obtained which would represent the ionization or δ-ray effect produced by a fixed number of α-particles, which is, strictly speaking, what should be given by an ionization curve. Nevertheless it does not seem advisable to use results thus obtained in the present investigation; the α-ray currents are small and the errors introduced by using them as factors might be considerable. Moreover, our purpose is primarily to compare the effects with different metals. The ionization curves of gases and vapours have also usually been obtained without allowance for the decrease in the number of α-particles, so that a more direct comparison with them is possible by using the curve I.b. An estimate of the number of δ-electrons due to one α-particle may be obtained, however, by dividing the abscissæ of I.b by those of II. Allowing for the fact that the charge on an α-particle is twice the electronic charge, we find that the number of δ-electrons per α-particle emitted by an aluminium plate from the incidence side only varies from 7 to 17 as the speed of the α-rays is gradually reduced.

One very striking result appeared in the course of these experiments which was quite unexpected from anything previously known as to the effects of α-rays. As the number of aluminium foils is decreased, the ionization follows a perfectly regular Bragg curve until only one thin foil is left. When, however, this is removed so that there is no obstacle between the polonium and the electrode, a very large increase is observed in the δ-ray current. Thus in the series represented by fig. 2, the δ-ray current for one thin foil is 7·82 while for no foils it is 16·27, an increase of 107 per cent. It has been shown that this is due to a very absorbable radiation consisting partly of electrons moving with considerably higher velocities than the hitherto recognized δ-rays. An investigation of this absorbable radiation will be described in the next section.

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* Proc. Roy. Soc. lxxxiii. p. 492 (1910).

Experiments similar to those which have been described at length in the case of aluminium were made also with copper, gold, lead, and platinum. In all cases the surfaces of the metals were made clean and bright by fine sandpaper. The magnitude of the δ-ray currents obtained from the various metals under similar conditions were not very different from each other, when correction was made for the decay of the polonium in the intervals between the experiments. The main purpose of the present investigation was to ascertain the variations in the *form* of the ionization curves for different metals and not their absolute magnitudes; for this reason no attempt was made to get an accurate determination as to the latter point. It is rendered difficult by the fact, discussed in § 1, that the δ-ray current falls off with the lapse of time after the liquid air has been applied to the charcoal. This effect was observed in all the metals studied, but it was not quite so marked as in the case of the thin platinum foil described in § 1. However, the diminution in the current sometimes amounted to as much as 20 per cent. and continued to be noticeable for two or three days[*]. As in the case of the platinum foil, the relative values at different points of the range of the α-particles were not affected by this variation, the ratio of the ionizations at any two points remaining practically constant.

The results for the different metals are given in Table III. and plotted in fig. 3. The values used are the currents due to the δ-electrons alone, corresponding to Curve I. *b* in fig. 2. In order to make the comparison easier they have been reduced to the same scale by making the current for one thick foil the same for all the metals; the other currents are then altered in the same ratio.

The points for the different metals lie so closely together that only one curve has been drawn. Anyone who has had experience with such measurements will recognize that the differences observed are too small to have any significance. Even in the case of aluminium, which appears to differ somewhat from the others, the differences are not at most more than 2 or 3 per cent.; and differences of this order, which are obviously accidental, occur in all the curves. We are

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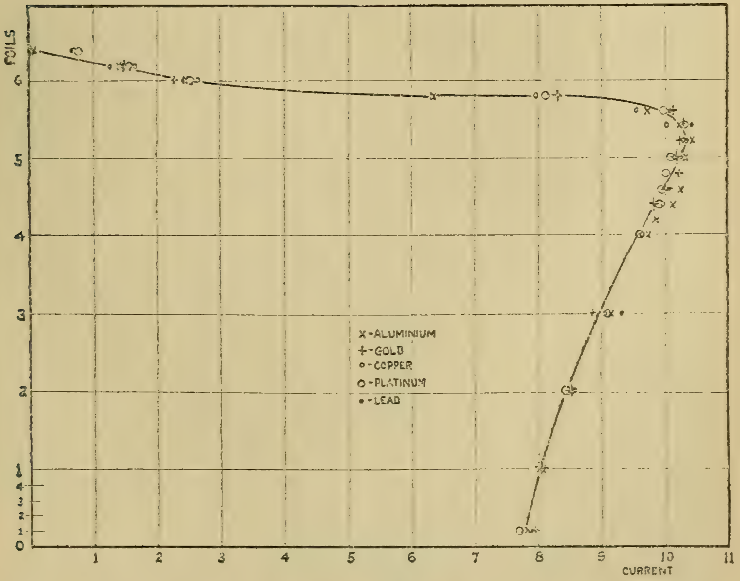
[*] Our observations in regard to the variations in the magnitude of the δ-ray current with different metals is in substantial agreement with those of Campbell, Phil. Mag. xxi. p. 298 (1911).

TABLE III.

Al. Foils Thick.	Al. Foils Thin.	Al.	Cu.	Au.	Pb.	Pt.
0	0	16·27	14·67	15·47	13·57	15·87
0	1	7·82	7·72	7·92	7·87	7·72
1	0	8·07	8·07	8·07	8·07	8·07
2	0	8·53	8·58	8·43	8·53	8·41
3	0	9·17	9·02	8·82	9·32	9·08
4	0	9·77	9·67	9·62	9·57	9·60
4	1	9·83	9·82			
4	2	10·12	9·92	9·82	9·85	9·90
4	3	10·24	9·99	9·99	10·04	9·94
4	4			10·05		10·00
5	0	10·31	10·16	10·19	10·26	10·11
5	1	10·45	10·25	10·25	10·35	10·25
5	2	10·21	10·00	10·31	10·41	10·26
5	3	9·71	9·56	10·11	10·06	9·96
5	4	6·35	7·95	8·30	8·30	8·15
6	0	2·45	2·65	2·29	2·41	2·51
6	1	1·43	1·73	1·56	1·25	1·61
6	2	·14	·77	·06	·73	·83

Fig. 3.



forced to conclude, therefore, that the ionization curves as observed, for all metals, have the same form. This is in agreement with the results of the less accurate experiments upon gold and aluminium described in the previous paper.

Whether or not the curves so obtained really represent the ionization of the metals is by no means certain. As has been said, the fact that there is no change in the form of the curve when its magnitude is considerably decreased by the removal of a surface-film of gas from the metal, makes it not improbable that the whole effect may be due to such a film. The probability of this explanation is increased by the fact that the ionization curves of gases and vapours do vary considerably; and it seems therefore unlikely that metals, so different in all their properties as those used above, should show such complete similarity in this respect.

§ 3. *Investigation of an Absorbable Radiation accompanying Alpha Rays.*

When the last thin aluminium foil is removed from the path of the α-rays, the number of electrons leaving the metal plate is greatly increased; this is shown by the first line of Table III. § 2. There appears to be, therefore, a very absorbable or "soft" radiation emitted by the polonium, which is completely stopped by $0{\cdot}64 \times 10^{-4}$ cm. of aluminium. To obtain an idea of the nature of this radiation, some experiments were made, in which we used the apparatus described in the previous paper *. It is substantially the same as that shown in figure 1 of the last section, except for slight differences in dimensions and the fact that there is only one disk to carry the aluminium foils, instead of two. A much stronger preparation of polonium, which we owe to the kindness of Professor Boltwood, permitted the use of an electrometer instead of an electroscope. A brass plate was used as the source of δ-rays, and the negative current from it was measured, with one thin foil interposed and with none, when various positive potentials were applied to the case ranging from 40 to 1000 volts. The results of these measurements are shown in fig. 4, where the abscissæ are the potentials applied to the case and the ordinates of Curves I. and III. are, respectively, the currents observed with one foil, and with no foils, interposed. The difference between the ordinates of the two curves shows the effect of the assumed soft radiation. This effect is greatly diminished as higher positive potentials are applied to the case, so that at 1000 volts it is reduced to about one-fourth of its value at 40 volts. This indicates that the radiation consists of electrons with much higher velocities than those attributed to the δ-rays, and with a wide range of velocities. As the positive potential on the case is increased, more and more of these electrons are withheld from reaching the brass plate. The fact that this radiation communicates a positive charge to the plate is not an obstacle to the hypothesis that it consists of electrons.

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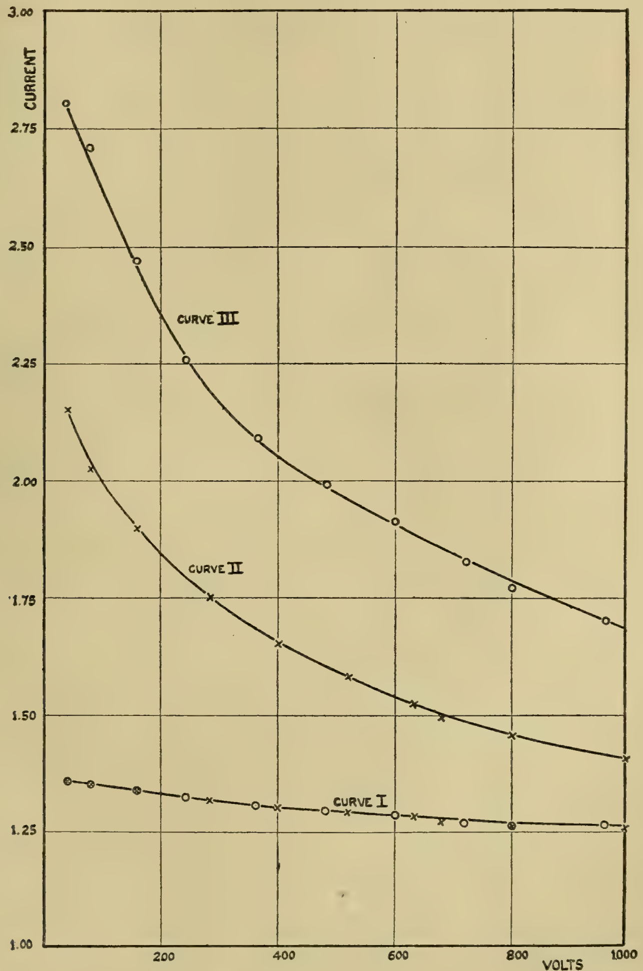
* Phil. Mag. xxii. p. 917 (1911); Am. Jour. Sci. xxxii. p. 413 (1911).

Fig. 4.



Since the early experiments of Lenard it has been known that electrons, moving with velocities corresponding to several hundred volts, when they fall upon a metal, cause the latter to emit secondary electrons, which may carry a larger negative charge away from the metal than it receives from the incident stream*.

It seemed possible that the diminution in the current with an increasing field might be due to an effect upon the electrons emitted by the plate, rather than upon the radiation itself—for example, by increasing the reflexion, or the number of secondary electrons from the case. In order to test this possibility, the brass plate (corresponding to E in fig. 1) was enclosed in a tin box, whose top was made of wire gauze in order to permit the α-rays and the new radiation to reach the plate. It was insulated from the case and could be charged by means of an external electrode. The box was kept charged to 40 volts while positive potentials up to 1000 volts were applied to the case; in this way the field in the vicinity of the plate, E, remained practically constant while the soft radiation had to pass through a variable field. The results were not essentially different from those shown in fig. 4.

In order to determine whether or not this soft radiation was peculiar to polonium, experiments were made in which the active deposit of thorium (obtained from a preparation of meso-thorium) was used. It was much less active than the polonium and more time was necessary for each reading; on account of the decay of the activity it was not practicable to wait until the changes due to the removal of the gas layer had ceased before beginning the readings. It was thus impossible to obtain as satisfactory numerical results as with the polonium, but there could be no doubt about the existence of the soft radiation. It produced a greater effect in proportion to that due to the α-rays than in the case of polonium; the ratio was about twice as great. On the other hand, the diminution produced by an opposing electrical field was not as great as with the polonium; with 940 volts on the case, the effect of the soft radiation was about one-half as great as with 80 volts. A similar change of potential with the polonium reduced the effect to one-third.

Returning to fig. 4, it will be observed that Curve I., which was supposed to be due to the α-rays alone, shows a diminution of the current as the potential on the case is increased, which is similar to that of Curve III. but much less in amount. This was at first difficult to explain; it is quite evident that the fields used were too small to accelerate the α-rays sufficiently to cause an appreciable decrease in the δ-ray current. The fact that the soft radiation accompanied the α-rays in the thorium deposit as well as in polonium suggested that it might be a secondary effect; if this were so, then the currents plotted in Curve I. (fig. 4) would be due not to the α-rays alone, but there would be a small admixture of the assumed secondary rays from the lower side of the aluminium foil on the disk *.

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* See also Gehrts, *Ann. d. Phys.* xxxvi. p. 1001 (1911), where it is shown that, when electrons with a velocity corresponding to 200 volts fall upon a copper plate, the secondary electrons carry away from the plate more than twice the charge brought to it by the incident electrons.

A small circle of the thicker aluminium foil, of the same diameter as the opening in the brass cylinder C (fig. 1) was pushed up against the polonium. In this way any soft radiation coming directly from the polonium would be stopped; but a secondary radiation due to the impact of the α-particles on the inner walls of the brass cylinder C would not be stopped unless a foil were interposed below the cylinder by means of the wheel. The experiment was made as before, by applying various positive potentials to the case and taking alternate readings with and without the foil below the cylinder.

The results are shown in Curve II. of fig. 4. The sensitiveness of the electrometer had changed by about 5 per cent. since the experiments with the uncovered polonium; the values of all the currents were reduced in the same ratio so that the measurements *with* the interposed foil should agree. In Curve I. the crosses represent the measurements when the polonium was covered, the circles those obtained when it was not covered, a thin foil being between the cylinder and electrode in both cases. A comparison of Curves III. and II. shows that the direct radiation contains a component which is much less affected by the retarding field than the secondary radiation alone. This agrees with the results of Wertenstein (*l. c.*) who, however, worked with a magnetic instead of an electric field. If we assume that the soft radiation is made up of two portions, one coming directly from the polonium, and not retarded by the field, while the other is secondary and consists of electrons, we may show by a simple calculation that the experimental results are accounted for in a very satisfactory manner.

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* At this stage of our experiments, the very interesting paper of Wertenstein, *Le Radium*, ix. p. 6 (1912), came to hand. By measuring the ionization due to RaC in gases at low pressures, he has demonstrated the existence of two soft radiations; one is secondary, and deviable in a magnetic field, and doubtless consists of electrons, while the other is not appreciably deflected in a magnetic field of 1100 units. The remainder of our work was done with a knowledge of Wertenstein's results and the next experiment was directly suggested by his paper.

Let a be the current of δ-electrons leaving the electrode due to the pencil of α-rays which strike it; this is present in all the curves. Let b be the current due to a soft radiation from the polonium which is unaffected by the field; this is present in III. but absent in I. and II. Let s be the current due to a secondary radiation (consisting of electrons), when there is no obstacle between the polonium and the electrode (Curve III.); this will vary with the electric field. The secondary radiation which produces s is due to nearly all the α-particles liberated by the polonium, through the complete solid angle 4π; but the secondary rays from the plug which carries the polonium and from the deeper parts of the cylinder are cut down by the limited aperture. When the polonium is covered, the secondary rays are due to the α-particles which emerge through a solid angle approximately equal to 2π; their effect will be equal to ms where $m<1$. (Curve II.). Finally, when the thin foil is interposed below the cylinder, the secondary rays from the lower side of the foil will be due to the α-rays which get out of the cylinder and pass through the foil; the solid angle in this case is about $0{\cdot}14\ \pi$, but the beam of secondary rays is not limited by any diaphragm. We may write ns $(n<m)$ for the δ-ray current produced in this case (Curve I.).

If, then, y_1, y_2, and y_3 are respectively the ordinates of Curves I., II., and III., we have,

$$\left.\begin{aligned} y_3 &= a+b+s \\ y_2 &= a \quad\ \ +ms \\ y_1 &= a \quad\ \ +ns \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a, b, m, n, are constants and s varies with the potential applied to the case. From these we obtain

$$(y_3-y_2) = b+\frac{1-m}{m-n}(y_2-y_1);$$

by plotting (y_3-y_2) against (y_2-y_1) from the curves in fig. 4, and drawing a straight line to represent the points as well as possible ,we obtain,

$$b = 0{\cdot}20\,; \quad \frac{1-m}{m-n} = 0{\cdot}62.$$

From an extension to 1700 volts of Curves I. and II. which was made later, we get as an approximate value of $\frac{n}{m}$, 0·15. This makes

$$m = 0{\cdot}65\,; \quad n = 0{\cdot}10.$$

With these values we may calculate s for different values of the potential on the case, from the curves, by the equations

$$s=\frac{y_2-y_1}{m-n}; \quad s=\frac{y_3-y_2-b}{1-m}.$$

The values of s given in the second column of Table IV. are means of the two values thus obtained.

TABLE IV.

$a = 1·24. \quad b = 0·20. \quad m = 0·65. \quad n = 0·10.$

Volts.	s.	y_3		y_2		y_1	
		obs.	calc.	obs.	calc.	obs.	calc.
40	1·39	2·82	2·83	2·15	2·14	1·36	1·38
100	1·20	2·63	2·64	2·00	2·02	1·35	1·36
200	0·90	2·35	2·34	1·85	1·82	1·33	1·33
300	0·71	2·16	2·15	1·74	1·70	1·31	1·31
400	0·60	2·05	2·04	1·65	1·63	1·30	1·30
500	0·54	1·98	1·98	1·59	1·59	1·29	1·29
600	0·48	1·91	1·92	1·54	1·55	1·28	1·29
700	0·41	1·85	1·85	1·50	1·51	1·28	1·28
800	0·34	1·78	1·78	1·46	1·46	1·27	1·27
900	0·29	1·73	1·73	1·43	1·43	1·27	1·27
1000	0·25	1·68	1·69	1·41	1·40	1·26	1·26

In this table the columns under "observed" are taken from the experimental curves; the columns under "calculated" are obtained from equation (1) with values of the constants given, and the values of s contained in the same line of the table. It is obvious that the relation between the three curves corresponds very closely to the hypothesis that, in addition to α-rays, a radioactive body emits a very absorbable primary radiation and that a secondary radiation consisting of moderately swift electrons is emitted by the source and also by any object which is struck by the α-rays.

This conclusion is in accord with the results of Wertenstein, who measured the ionization produced in air at low pressures by the radiations from RaC, when the distance between the source and the ionization-chamber was varied. He attributes the soft primary radiation to the recoil atoms of RaD, and it seems very probable that this view is correct. His results differ from ours, however, in the relative magnitudes of the effects of the different types of rays. Thus he states (*l. c.* page 19) that in a narrow ionization-chamber and with a clean active surface, the soft primary rays (recoil atoms) may make five times as many ions as the α-rays. In our experiments the current of δ-electrons produced by the soft primary radiation is only $\frac{1}{6}$ of that produced by the α-rays. This discrepancy is due, at least in part, to the fact that the deposit of polonium which we used could not be regarded as "thin" in regard to this very absorbable radiation. Wertenstein found that this radiation could be considerably increased by depositing the Ra C upon a platinum plate, and thus avoiding a film of oxide which formed on other metals under the action of the radium emanation. Another cause for the difference is probably to be found in the fact that his experiments were made at pressures of from 3 to 10 mm. instead of in a high vacuum; in the latter case, fewer of the recoil atoms are charged, and their ionizing effect might be expected to be less.

On the other hand, the ionizing effect of the secondary rays in his experiments was small, amounting only to about $\frac{1}{5}$ of the α-ray effect, whereas our results show that it causes the emission of 1·12 times as many δ-electrons as the α-rays. It is true that these results depend upon the dimensions of the cylinders which are used to limit the pencil of α-rays, but it seems scarcely possible that so large a discrepancy can be attributed to this cause. It may be that the secondary rays are more efficient in causing the liberation of δ-electrons from the metals than in ionizing a gas; it may be also that the transverse magnetic field used by Wertenstein to deflect these rays from his ionization-chamber was not altogether effective in the presence of air which was necessary for ionization measurements.

The values of s in the second column of Table IV. give some idea of the distribution of velocities among the secondary electrons, but no numerical results can be conveniently deduced from them. The number of secondary (in this case tertiary) electrons emitted by a metal when struck by a moving electron changes rapidly with the speed of the moving electron, especially within the range of velocities with which we have to do in this case*. It will probably not be difficult, however, to determine the velocity distribution by using a Faraday cylinder as the recipient of the rays.

It is evident that the range of velocities extends from less than $3{\cdot}8\times10^8\frac{\text{cm.}}{\text{sec.}}$, which corresponds to 40 volts, to more than $18{\cdot}8\times10^8$, which corresponds to 1000 volts. An experiment, not here reported in detail, showed that there was still a very appreciable effect from the secondary radiation with an opposing potential of 1700 volts; this corresponds to a velocity of $24 \cdot 4 \times 10^8$. This is not far from the maximum estimate which Wertenstein obtained with the magnetic field, viz. $2 \cdot 3 \times 10^9$.

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* See Gehrts, *Ann. d. Phys.* xxxvi. pp. 1003 *et seq.* (1911).

It is plain that the existence of this radiation vitiates the estimates which have hitherto been made of the velocities of the slow δ-electrons. Thus, for example, an insulated source of α- and δ-rays, within an earthed enclosure, will lose more swift electrons than it gains from the enclosure; its potential will rise until it can attract enough slow electrons to balance this loss. The value of this steady potential will not depend on the speed of the slow electrons so much as upon the size and shape of the enclosure in relation to the insulated source. If, as in Campbell's experiments [*], the apparatus is arranged so that all the electrons from either of two electrodes A and B strike the other one, there is still a complication which renders impossible any simple interpretation of the results. Comparatively slight changes[†] in the velocity of the swift secondary electrons from A, for example, may alter considerably the number of slow tertiary electrons emitted by B. Thus false balances may be obtained which have little relation to the speed of the slow electrons. In fact it seems possible that the difficulties which Campbell encountered when one of his electrodes was covered with soot [‡], and which led him to adopt the hypothesis that the δ-electrons had no appreciable velocity, may be accounted for in this way.

When a metal is struck by α-rays it is evident that some, at least, of the slow δ-electrons which result are not due to the direct action of the α-rays, but are produced through the intermediary of the swifter secondary electrons generated in the metal itself near its surface. The question naturally arises whether the whole of the effect may not be produced in this indirect way. A consideration of the results exhibited in Curve I. of fig. 4 shows that this is not beyond the bounds of possibility. In this experiment we have secondary rays produced by the same pencil of α-rays at two places—the aluminium foil on the wheel and the plate corresponding to E, fig. 1. The δ-ray current from the plate due to the α-rays is 1·24; let us assume that it is produced as indicated above. The current produced by the secondary rays from the foil (with 40 volts on the case) is

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[*] Phil. Mag. xxi. p. 280 (1911).

[†] See Gehrts, *l. c.*

[‡] Phil. Mag. xxiii. pp. 54 *et seq.* (1912).

$ns = 0{\cdot}14$; the ratio of these currents is 0·11. Now the plate subtends at the foil a solid angle of $4\pi \times 0{\cdot}15$ *: for an electron generated in the plate itself we may take the solid angle as 4π. Taking the figures as they stand, this would indicate that at least $\frac{1}{15}$ of the supposed α-ray effect is produced indirectly by means of the secondary electrons generated in the plate. We may suppose that they give rise to the slow electrons, either as they emerge from the plate itself, or as they pass through the layer of gas which we have been led to postulate by the results of the preceding section.

If this should prove to be the mechanism of the emission of δ-rays by metals, it will at least render it probable that a similar process takes place when gases are ionized by α-rays. The column of ions following the track of the α-particle, which was assumed by Moulin, and which has recently been made visible in the beautiful experiments of C. T. R. Wilson, would then be made up of the tracks of many secondary electrons, radiating irregularly from the axis of the column, and extending only a small fraction of a millimetre from it.

Summary.

1. The number of δ-electrons emitted by a metal when struck by α-rays varies with the speed of the α-rays in the same manner as does the number of ions produced in a gas. Curves which represent this variation are similar in form to the Bragg ionization curve.

2. Such curves have been determined for aluminium, copper, gold, lead, and platinum. Within the limits of accuracy of the experiments they have the same form for all these metals; this agreement is in contrast with the fact that ionization curves for different gases and vapours show marked differences in form.

3. The magnitude of the δ-ray effect, and the field necessary to cause saturation, decrease progressively for some time after the vacuum is produced. This is ascribed to the gradual removal of a layer of adsorbed gas; during this process the *form* of the "ionization curve" does not change. This suggests that the whole effect may be due to such a layer which cannot be entirely removed; the similarity of the curves obtained with different metals would thus find a natural explanation. However, an experiment, in which a strip of platinum was heated to red heat in a high vacuum, failed to give evidence of the removal of this assumed film.

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* The dimensions are different from those shown in fig. 1.

4. Polonium and the active deposit of thorium emit a radiation which is completely absorbed by $0{\cdot}64\times10^{-4}$ cm. of aluminium. This radiation causes the emission of electrons from metals which it strikes. It consists of two portions, one of which is primary and not appreciably affected by an electric field; the other is secondary and consists of electrons whose velocities range from less than $3{\cdot}8\times10^{8}$ to more than $24{\cdot}4\times10^{8}\frac{\text{cm.}}{\text{sec.}}$. Wertenstein has found that RaC emits similar soft radiations, which ionize a gas; he attributes the primary radiation to the recoil atoms.

5. The secondary radiation is emitted not only by the source, but by any object on which α-rays are incident. The electrons of which it consists have considerably higher velocities than the δ-rays hitherto recognized.

6. A part, at least, of the ordinary δ-radiation is due, not to the direct action of the α-rays, but to these secondary rays. So far as can be concluded from the present experiments, it is quite possible that the whole of the δ-ray effect may be thus produced.

Sloane Laboratory, Yale University,
June 4, 1912.

XLV. *The Law of Molecular Attraction.*
By J. E. MILLS *.

DR. R. D. KLEEMAN at first † proposed an inverse fifth power law of molecular attraction. It was pointed out ‡ that this law was not at all in agreement with the facts, and he then claimed § that an inverse seventh power law gave an equation,

$$\frac{\mathrm{L}-\mathrm{E}_e}{d^2-\mathrm{D}^2}=\text{constant}, \quad . \quad . \quad . \quad . \quad (1)$$

which was in as good agreement with the facts as an equation,

$$\frac{\mathrm{L}-\mathrm{E}_e}{d^{1/3}-\mathrm{D}^{1/3}}=\text{constant}, \quad . \quad . \quad . \quad . \quad (2)$$

derived by the author from an inverse square law of attraction. In these equations $L-E_e$ is the internal heat of vaporization, and d and D are the densities of liquid and vapour respectively.

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* Communicated by the Author.
† Phil. Mag. xix. p. 795 (1910).
‡ Mills & MacRae, Journ. Amer. Chem. Soc. xxxii. p. 1175 (1910).
§ Phil. Mag. xx. p. 678 (1910).

It is fortunately possible to test the correctness of Kleeman's statement by reference to the facts. Prof. Sydney Young in 1903 wrote me that he considered benzene, fluorbenzene, normal pentane, normal hexane, and isopentane as probably yielding the best experimental results among the substances measured. For testing Kleeman's equation I therefore chose the three of the above substances of different type, and in addition ethyl oxide and carbon tetrachloride as representing other types of compounds. The data used are completely given by Young [*]. I give the results of the test of both my own and Kleeman's equation below (pp. 486--487). The average of the constant was in each case taken to the line drawn, and all divergences greater than 2 per cent. from this average are marked by an asterisk above and to the right. My equation gives for these five substances two divergences from the average value of the constant greater than 2 per cent. Kleeman's equation gives with isopentane 6 such divergences, with normal pentane 5, with ethyl ether 9, with benzene 15, with carbon tetrachloride 12. But this is not all. My equation gives for the entire 26 non-associated substances measured by Young and his co-workers not a single divergence [†] greater than 2 per cent. from the mean value of the constant given, except as introduced by known errors occurring at 0° C. (30° for bromo-benzene) near the critical temperature, and for di-isobutyl, all as noted below. From the average values of the constants there given my equation shows for these 26 substances within the limits stated divergences greater than 2 per cent. only for chlorobenzene at 130° (2·15 per cent.), carbon tetrachloride at 250° and 260° (see above), and ethyl propionate at 100° (2·1 per cent.). The last line on p. 91 of the article just cited should read "more than 1 per cent. from the average values are marked above and to the left with a." Kleeman's equation, as shown more fully below, in no case investigated gives results which can possibly be regarded as within the limit of the experimental error of the measurements involved.

Near the commencement of my work upon molecular attraction some eight years ago I discussed [‡] the way in which the various errors of measurement would affect the constant. For a discussion of the errors of measurement themselves, see Young *. I at that time adopted 2 per cent. as the probable allowable limit of divergence in the constant due to the errors of measurement as compounded and multiplied in their effect upon the constant, and Dr. Young, who with his co-workers made the measurements, acquiesced. At that time my own results showed many divergences in the constant greater than 2 per cent. from the mean value. I set about finding the reason for these divergences, and as the statement has been made that my equation is probably accidental, I would like to call attention to some of the really remarkable "accidents" that have happened in the course of my investigation.

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[*] Sci. Proc. Roy. Dublin Soc. xii., June 1910.

[†] Phil. Mag. July 1911, p. 84.

[‡] Journ. Phys. Chem. viii. pp. 392-397 (1904).

1. *Ethyl oxide.*—Unusual variations in the "constant" at and above 185° caused me to suspect an error in the heats of vaporization as calculated by Ramsay and Young. Young repeated the calculations at my suggestion and corrected the error †.

2. *Di-isobutyl* showed some divergent values of the constant which resisted explanation. Finally, in 1906, I wished to measure the substance further, and Dr. Young very kindly agreed to let me have the original substance. On getting the liquid, which had been very carefully preserved in a well-stoppered bottle, small crystals were found in the bottom of the bottle. On pouring off the liquid and attempting to fractionate it, further crystals appeared in the Young's fractionating column and even in the condenser-tubes, the boiling-point of the liquid meanwhile remaining apparently constant. This remarkable fact caused Dr. Young to say that possibly the liquid was impure when measured, a remark he has since taken care to repeat ‡. I was not able to purify the liquid and could not at the time prepare more, so that no further measurements were made.

3. *Stannic chloride.*—The divergences first found, which I originally thought must be due to some decomposition of the substance, were later shown to be due to an error in my own calculations.

4. *Chloro-benzene.*—To explain certain divergences at 240° to 270° I suggested in 1904 § that the Biot formula used for obtaining the $\frac{dP}{dT}$ was probably wrong. This explanation was shown some five years later to be correct when Young himself recalculated the formula.

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* Sci. Proc. Roy. Dublin Soc. xii. No. 31 (1910).

† Journ. Phys. Chem. viii. p. 635 (1904).

‡ Sci. Proc. Roy. Dublin Soc. xii. No. 31, p. 384 (1910).

§ Journ. Phys. Chem. viii. p. 400 (1904).

Temp.	Ethyl oxide.		Normal pentane.		Isopentane.	
	$\frac{L-E_e}{d^2-D^2}$	$\frac{L-E_e}{d^{1/3}-D^{1/3}}$	$\frac{L-E_e}{d^2-D^2}$	$\frac{L-E_e}{d^{1/3}-D^{1/3}}$	$\frac{L-E_e}{d^2-D^2}$	$\frac{L-E_e}{d^{1/3}-D^{1/3}}$
Average constant...	161·4	103·76	212·2	109·94	201·4	105·46
0° C. ...	157·6*	105·6	206·1*	111·1	199·6	107·2
10	157·7*	104·8	—	—	194·8*	104·5
20	157·2*	103·9	—	—	197·1*	105·1
30	157·3*	103·4	204·8*	108·6	198·2	105·1
40	157·8*	103·0	207·2*	109·4	198·3	104·8
50	158·8	102·9	208·1	109·3	198·8	104·7
60	158·9	102·9	209·5	109·6	199·0	104·5
70	159·0	102·7	210·5	109·7	199·4	104·4
80	159·6	102·9	211·5	109·8	200·8	105·0
90	161·1	103·2	212·4	109·9	202·3	105·4
100	162·2	103·6	213·1	110·0	203·9	105·9
110	163·2	103·8	214·7	110·5	204·3	106·0
120	164·6	104·1	216·6*	111·1	205·1	106·3
130	165·9*	104·6	216·6*	111·0	205·9*	106·5
140	167·1*	105·0	215·6	110·5	206·5*	106·7
150	167·1*	105·1	216·0	110·5	206·6*	106·9
160	165·9*	104·6	215·6	110·3	206·2*	106·7
170	163·8	103·5	215·6	110·3	203·0	105·5
180	161·6	101·9	213·2	109·3	197·4	103·4
190	153·6*	97·4*	205·8	106·3*	—	—
—	—	—	—	—	—	—
—	—	—	—	—	—	—
—	—	—	—	—	—	—
Critical temperature...	193°·8		197°·2		187°·8	

Temp.	Benzene.		Carbon tetrachloride.	
	$\frac{L-E_e}{d^2-D^2}$	$\frac{L-E_e}{d^{1/3}-D^{1/3}}$	$\frac{L-E_e}{d^2-D^2}$	$\frac{L-E_e}{d^{1/3}-D^{1/3}}$
Average constant ...	134·1	109·26	197·2	44·01
0° C.	122·4*	108·3	181·4*	43·5
70	129·6*	108·7	189·9*	43·5
80	130·7*	109·2	191·0*	43·5
90	131·0*	109·1	192·2*	43·6
100	131·1*	108·7	192·7*	43·5
110	131·2*	108·3	193·1*	43·5
120	130·8*	107·6	193·9	43·5
130	131·8	107·9	194·3	43·4
140	132·7	108·2	195·1	43·5
150	133·6	108·5	196·0	43·5
160	134·7	109·1	197·6	43·8
170	135·8	109·4	198·9	44·0
180	136·9*	110·1	198·6	43·9
190	137·2*	110·1	199·1	44·0
200	137·3*	110·1	200·5	44·2
210	138·5*	110·7	201·7*	44·3
220	138·3*	110·5	202·8*	44·5
230	138·1*	110·4	203·9*	44·8
240	138·0*	110·4	204·9*	44·9
250	138·2*	110·5	205·6*	45·2*
260	137·5*	110·2	204·4*	45·0*
270	135·9	109·3	201·0	44·5
280	133·1	107·8	196·3	43·9
Critical temperature...	288°·5		283°·15	

5. *Bromo-benzene* showed divergences at 30° and at 160° and 170°. I thought these errors due to the Biot formula and to the vapour-density *. Later these errors were greatly reduced by a recalculation of the Biot formula by Young, and by the slight revisions made by Young in some of the volumes of the saturated vapour. At 30° the value still differs from the mean by more than 2 per cent. At this temperature the vapour-pressure has a value of only 5·67 millimetres of mercury, and the $\frac{dP}{dT}$ is but a fraction of a millimetre. It can be easily seen that one could not hope to obtain with any degree of certainty the true value (within 2 per cent.) of the $\frac{dP}{dT}$ from the Biot formula at this, its end point. The calculated vapour-density is also used, and this introduces some error.

6. *Iodo-benzene.*—I thought the divergences at 190° to 210° to be due to the vapour-density (volume) and so stated †. Later Young's revisions showed these errors to be largely due to the vapour-density but partly also to the Biot formula.

7. *Methyl formate.*—In 1906 ‡ I stated that the divergences at 30° and 40° were probably due to the vapour-density. Later, Young resmoothed these values and the divergences disappeared. A change in the value of the mean likewise caused the divergence at 180° to decrease to within the 2 per cent. limit.

8. *Ethyl acetate.*—A change in the average due to the revision of the vapour-density by Young caused the divergences at 220° and 230° to come within the 2 per cent. limit.

9. *Methyl isobutyrate.*—At 130° a misprint of 105 for 103 in the volume of the vapour was found by Dr. Young § upon examining the original manuscript at my request, and a corresponding "divergence" in the constant disappeared. Other misprints were found in the course of my work, but I shall always consider the discovery of this particular misprint an unusual achievement had it been accomplished by the use of a merely "accidental" relation. Recalculation of the Biot formula and resmoothing of the vapour-density by Young also caused the divergence at 260° to come within the 2 per cent. limit.

10. The values at 0° C. were often high. This was known all along to be due in part to the use of the calculated density

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* Journ. Phys. Chem. viii. p. 400 (1904).

† *Ibid.* viii. p. 401 (1904).

‡ *Ibid.* x. p. 18 (1906).

§ *Ibid.* xi. pp. 621–622 (1907).

of the vapour, direct measurements being not usually available at this point. The same is true of bromo-benzene and iodo-benzene at 30°. The error so caused can be estimated by a method pointed out by Young *, and I give below the probable amount of the error thus introduced.

	Reduced. temp.	Error.		Reduced temp.	Error.
		per cent.			per cent.
Di-isopropyl	0·55	1·5	Carbon tetrachloride..	0·49	0·7
Di-isobutyl	0·50	0·9	Stannic chloride	0·46	0·5
Isopentane...............	0·59	2·2	Methyl formate	0·56	1·7
Normal pentane	0·58	2·0	Ethyl formate	0·54	1·4
Normal hexane.........	0·54	1·4	Methyl actate	0·54	1·4
Normal heptane	0·51	1·0	Propyl formate.........	0·51	1·0
Normal octane	0·48	0·6	Ethyl acetate............	0·52	1·1
Hexamethylene.........	0·49	0·7	Methyl propionate ...	0·51	1·0
Benzene	0·49	0·7	Propyl acetate	0·50	0·9
Fluor-benzene	0·49	0·7	Ethyl propionate	0·50	0·9
Chloro-benzene.........	0·43	Very little	Methyl butyrate	0·49	0·8
Bromo-benzene at 30°.	0·45	,, ,,	Methyl isobutyrate ...	0·505	0·9
Iodo-benzene at 30°...	0·42	Nearly correct			

These errors cause practically the same percentage errors in the heats of vaporization and in the constants, making them too large. After making these corrections the values of the constants at 0° are apparently as much below as above the average. Further rather large variations at this point are caused by the necessary uncertainty in obtaining the $\frac{dP}{dT}$ from the Biot formula at and near its end point. The vapour-pressure is here very small, and the $\frac{dP}{dT}$ sometimes only a fraction of a millimetre, and the multiplication of the percentage error is therefore enormous.

11. Some few misprints which it is not thought necessary to detail were brought to light during the close scrutiny to which the measurements were subjected.

12. As the critical temperature was approached, the constant of my equation showed a large and persistent decrease for all substances, not accounted for by any facts that were known when I began my work. I devoted much time to a study of these divergences and was led to the discovery of three new facts.

First.—At and near the critical temperature the values of the vapour-pressure calculated from Young's Biot formulæ were never in exact accord with the observed vapour-pressures, the observed vapour-pressures being with one or two exceptions greater than the calculated. The difference was insignificant when compared with the total vapour-pressure, but occurred rather suddenly, thereby altering the trend of the vapour-pressure curve and causing very serious errors in the $\frac{dP}{dT}$ calculated from the Biot curve. This fact was discussed at length in my fourth paper [*], and it was clearly revealed later that no possible recalculation of the Biot formulæ constants *could possibly* make the calculated values of the vapour-pressure fit the observed values in the immediate neighbourhood of the critical temperature. Young has recognized this point and called attention to it [†].

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* 'Stoichiometry,' p. 342.

Second.—I noted [‡] that the values of k for the critical isochors which Young and his co-workers had obtained for isopentane, normal pentane, and ether, must be identical with the $\frac{dP}{dT}$ of the saturated vapour at the critical temperature. Young acknowledged this fact and has called public attention to it [§]. The discovery was extremely fortunate, for it gave fairly accurate values for the $\frac{dP}{dT}$ at the critical point for three substances. The limit of the equation

$$\frac{L-E_e}{d^{1/3}-D^{1/3}} = \text{constant}$$

at the critical temperature as d approaches D in value is,

$$3V_c^{4/3} \times 0{\cdot}0_4 31833 \left(\frac{dP}{dT}T-P\right) = \text{constant}, \quad . \quad . \quad (3)$$

and the values of the constants for the three substances mentioned then come out as follows :—

	Using $\frac{dP}{dT}$ from Biot formula.	Using $\frac{dP}{dT}$ from k.	Using $\frac{dP}{dT}$ from $\frac{2R}{V_c}$	Average of values at lower temperatures.
Isopentane.........	95·5	107·2	107·05	105·46
Normal pentane..	97·3	111·1	109·4	109·94
Ethyl oxide	90·5	100·4	102·0	103·76

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[*] Journ. Phys. Chem. vol. ix. p. 402 (1905).

[†] 'Stoichiometry,' pp. 129-130.

[‡] Journ. Phys. Chem. viii. p. 594 (1904). k is in that paper called b, following Ramsay and Young's original nomenclature.

[§] 'Stoichiometry,' p. 213.

Third.—I further found [*] that, if Crompton's equation was true, the $\frac{dP}{dT}$ at the critical temperature was equal to $2R/V_c$. I give the corresponding values at the critical temperature of the constant so obtained above. This relation I later found had earlier been noted as an empirical fact by Dieterici [†].

So finally, excepting the values at 0° C. (30° for bromobenzene and iodobenzene) and near the critical temperature, and di-isobutyl, every single divergence greater than 2 per cent. from the mean value of the constant for the remaining 25 non-associated substances measured by Young and his co-workers was found to be due to errors and *removed.* The divergences at 0° and near the critical temperature and for di-isobutyl were satisfactorily explained. I now have the satisfaction of knowing that, within the limits above stated, 8 of the 25 substances show not a single divergence of the constant greater than 1 per cent. from the average value, and that there are only 17 divergences over 1·5 per cent. out of a total of 431 comparisons, and these divergences occur where known errors of observation and calculation are greatest.

I have been asked to believe that this equation is an accident. My answer is that years of labour have shown that where there were originally material discrepancies between the equation and the measurements, these discrepancies were not due to the inaccuracy of the equation. The equation stands today in complete accord with the facts.

I would remark that in not a single instance was any error corrected, or any measurement smoothed, or Biot formula recalculated, except by Dr. Young himself; and probably when the revised values were sent me by Dr. Young he has never in a single instance (except where mere misprints were corrected) been able to foresee whether his revisions would benefit or injure the "constant" that I was to obtain from their use. In revising the volumes (densities) of the saturated vapour, and in recalculating some of the Biot formulæ, Dr. Young had other reasons than those given above for undertaking the revision, and the fact that I had previously in some instances suspected that such revision was desirable was only incidental. Dr. Young has himself collected and republished [‡] the complete revised data that I have used.

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[*] Journ. Phys. Chem. vol. ix. p. 402 (1905).

[†] *Ann. der Physik,* xii. p. 144 (1903).

[‡] Sci. Proc. Roy. Dublin Soc. xii. No. 31 (1910).

I am deeply indebted to Dr. Young for the assistance which he has most kindly given me during the progress of my work. The casual reader will hardly appreciate the immense labour involved in locating and removing the errors mentioned in this paper. But I hope that he will understand that their discovery and removal was not the result of accident and could not have been accomplished had the relation which served as my guide been a mere approximation—itself the result of an accident.

Is the equation *exactly* true? It agrees with the facts at present known as accurately as the corresponding measurements have been made, and it is fortunate that they have been made with wonderful accuracy. But in my opinion, the equation has a theoretical significance and could only be exactly true with absolutely stable and absolutely non-associated substances. We have liquids nearly fulfilling these conditions from 0° C. to their critical temperature, but the esters and some of the other substances measured will probably not be found exactly to fulfil this condition throughout so wide a range of temperature.

Considering the constant of Kleeman's equation,

$$\frac{L-E}{d^2-D^2}=\text{constant},$$

more closely, it will be noted that for isopentane, certainly one of the most carefully measured of the substances, the constant increases from 194·8 at 10° to 206·6 at 150° (the high value at 0° is due to the use of the *calculated* vapour density), or an increase of 6 per cent. There is a similar increase with the other substances.

Now if a diagram of the $L-E_e$ and density lines for isopentane be made, it will be seen that the $L-E_e$ line is approximately straight to 120° C. as is also the line for the density of the liquid. Now at 120° d^2 for isopentane is 0·2491 and D^2 is 0·0010. Therefore up to and below 120° D^2 is practically negligible compared with d^2. Throughout this temperature interval Kleeman's equation practically reduces to

$$\frac{L-E_e}{d^2}=\text{constant}.$$

Now while there are small individual errors in $L-E_e$ the trend of the line is certainly most accurately established. The errors in d, and consequently in d^2, are *very small.* Hence the steady increase shown by the constant of

Kleeman's equation for this substance is unquestionably due to the fact that his equation *does not* represent the facts. A similar examination of the other substances tested will compel the same conclusion.

Regarding the tests made by Kleeman of his relation, I would say that he used the unrevised data given in my earlier papers. His tests are therefore not as correct as it is possible to make them. His own tests do, however, when the substances measured by Young are considered, completely bear out the statement here made that his equation does not represent the facts. In the light of the results he gives I do not see how it was possible for him to claim that the equation

$$\frac{L-E_e}{d^2-D^2}=\text{constant}$$

is as accurate as

$$\frac{L-E_e}{d^{1/3}-D^{1/3}}=\text{constant}.$$

Also I would point out that I had *previously* investigated [*] the important equation of Dieterici for all of the substances which Kleeman examines. And the relation between Dieterici's equation and mine which Kleeman points out in later papers, had already been discussed either by Steinhaus [†] or by myself [‡].

Kleeman further states [§] that an infinite number of equations must exist giving true relations between the heat of vaporization and the density of a substance, and therefore that the law of molecular attraction cannot be deduced from any such relation. Several different phases of this position should be clearly understood.

1. It is impossible to get more out of a mathematical process than we put in. This is universally admitted, and Kleeman's conclusions, if correct, must be as he states, a consequence of the nature of the heat of evaporation.

2. When one simply measures the heat of vaporization of a given substance under a given set of conditions, there is no *a priori* method of finding out what that heat went to do. Were it not for other known facts one might suppose that there was no attraction whatever between the molecules and that all of the heat was expended in pushing back the external pressure. This hypothesis is readily disproved, and the amount of energy that was actually used in pushing

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[*] Journ. Am. Chem. Sci. xxxi. p. 1099 (1909).

[†] *Studien zum Problem der Zustandsgleichung*, p. 38, etc.

[‡] *Loc. cit.*

[§] Phil. Mag. xx. p. 901 (1910) and later articles.

back the atmosphere is readily calculated. There is a surplus. Again there is no *a priori* method of deciding whether any or all of that surplus actually did go to overcome molecular attraction. It might have been used to increase the kinetic energy of the individual molecules. It might have been used—in part at least—to effect certain chemical changes, or other interatomic actions. If no other fact be taken into consideration, and no hypothesis be allowed, it clearly would be impossible to determine how much energy went to overcome molecular attraction, and consequently the actual law of the attraction could not be determined.

In a search for the true law of molecular attraction from among the infinite suppositions which a complete ignorance of the facts would make possible, two limitations exist and should serve as a guide to our work. These are mentioned below.

3. The first limitation might be called the simplicity of nature. The numerous compounds in the universe are made up of perhaps about eighty elements. These elements, it is very probable, are themselves composed of one or more very much simpler bodies. These bodies have doubtless certain properties as to shape, size, motion, &c., and the intricacy of things as we see them is produced doubtless from the action of a very few simple laws. The motions of the planets are complex, but the laws that cause these motions are very simple. The very fact that we search for a law of molecular attraction (instead of supposing that each attraction is different) is itself a recognition of the simplicity of nature.

Has not Kleeman perhaps lost sight of the probable simplicity of nature when he produces* as his fundamental equation for the heat of vaporization, L, the following relation :—

$$\mathrm{L}=\frac{(\Sigma\sqrt{m_1})^2}{m}x_a\left[\underset{n,\,w,\,u,\,v}{\int,\ \Sigma}\right]\cdot\phi_2\left(\frac{z_1}{x_c},\frac{\mathrm{T}}{\mathrm{T}_c}\right)\cdot\frac{x_a(n+w)}{{z_1}^6}$$

$$-\frac{(\Sigma\sqrt{m_1})^2}{m}x_b\left[\underset{n,\,w,\,u,\,v}{\int,\ \Sigma}\right]\cdot\phi\left(\frac{z_2}{x_c},\frac{\mathrm{T}}{\mathrm{T}_c}\right)\cdot\frac{x_b(n+w)}{{z_2}^6}\quad.\qquad(4)$$

where

$$z_1=x_a\sqrt{\{(n+w)^2+u^2+v^2\}},$$

and

$$z_2=x_b\sqrt{\{(n+w)^2+u^2+v^2\}}.$$

It is not necessary to explain the meaning of the symbols.

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* Phil. Mag. October 1911, p. 567.

The expression for the internal heat of vaporization, λ, as actually deduced by the author and shown to be in accord with the facts, is,

$$\lambda = \text{constant } (\sqrt[3]{d} - \sqrt[3]{D}).$$

Here we only desire to contrast the equations as to simplicity, remembering that such a test is justified by our knowledge of nature and her laws. I do not mean to be unfair to Kleeman. His equation is a general one, and under certain conditions would, I think, reduce to mine. I do mean to say that in my opinion the fundamental laws of nature will prove to be simple, and that they can be represented simply when they are understood.

4. The second limitation is the limitation imposed by the facts which it is possible to connect with the problem. By making what I considered legitimate use of known facts, I have escaped many difficulties and could approach a solution of the problem of molecular attraction in a relatively simple manner.

5. I certainly agree that if we were completely ignorant of other facts than a knowledge of the heat of vaporization it would be impossible to deduce the law of molecular attraction. But Kleeman apparently admits, or tentatively admits, that our knowledge enables us to connect the internal heat of vaporization, λ, with the changes in density of the substance ρ according to an equation,

$$\lambda = \psi(\rho) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From this fact alone—the fact that the internal latent heat is some function of the density of the substance—Kleeman deduces the statement that the internal heat and the density of a substance can be connected by an infinite number of equations.

It is perfectly true that both sides of equation (5) can be multiplied or divided by the same quantity, or increased or diminished by the same quantity, and thus an infinite number of equations can be obtained. But these equations are all identical, and it would certainly be misleading to speak of them as an infinite number of equations connecting the same two quantities.

Moreover, a transformation of coordinates could be made, or other changes could be made in our symbols of expression, and thus the relation between ρ and λ could be expressed in various ways. But no one can claim that the relation between ρ and λ is changed, or that other relations between ρ and λ exist, merely because we change our symbols for expressing a certain relationship which they actually do possess.

Again, it is possible to approximate any simple curve more or less closely by a number of quite different equations. Thus the vapour-pressure curve has been approximately reproduced by various equations. But these equations for the most part make no attempt or pretence to represent nature. So far from all of them being true they are none of them exactly true. If one could be found exactly true, then its variables and constants would have a more than mathematical significance; that is, they would represent certain variables and constants of nature which we might say "determine" the vapour-pressure curve. If Kleeman means that as a mathematical exercise he can produce by the use of arbitrary constants various equations connecting the densities and internal heats of vaporization with an approximation to the truth, I will grant it. But if he means that in my work I have overlooked a constant of integration I think he is wrong.

Considering equation (5) as representing *per se* the relation between the internal heat of vaporization and the density of the substance, it is clear that from equation (5) *alone* it is impossible to deduce the fact that an infinite number of different relations exist between ρ and λ. *Because such a deduction would place us in the position of being able to prove that because one relation existed between two quantities, an infinite number of relations must exist between the same two quantities.*

6. It remains to locate the exact errors in Kleeman's proof of his position. Without quoting his proof, and proceeding on the supposition that it is available to those interested in locating the error, I deal first with the proof when the internal heat of vaporization L is expressed as a function of the density of the liquid and the temperature according to the equation $L=\psi_2(\rho, T)$. (Kleeman's symbols are used in this section.) Kleeman's first step is to draw a curve A_1A_2 (fig. 1) to represent this equation at the temperature T_1. Now as a matter of fact for a particular substance, at a particular temperature, there is but one value of the heat of vaporization and *Kleeman's curve should be a point.*

Considering next the proof when $L=\psi_2(\rho)$, and $A_1'A_2'$, fig. 2, its graph. Kleeman then says: "Let the difference between the ordinates c_1a_2, b_1, b_2 denote the latent heat of a liquid corresponding to the temperatures T_1, T_2 . . . . . etc." Since there is in reality a relation between ρ and T (a relation none the less real because it is not given in the above equation) I do not see that the above supposition is legitimate. The difference between the ordinates named, as I see it, might not denote the latent heat of the liquid corresponding to the temperatures named. I think that there are further objections to the proof given, but it seems to me that the one named is sufficient.

I do not see any reason to suppose, nor any way to prove, that an infinite number of true and yet different relations exist between L and ρ as a matter of reality, and if relations are found mathematically which do not exist in reality the fault is with the mathematics.

7. The actual facts, it seems to me, are precisely the reverse of the condition for which Kleeman is arguing. If in nature there are two phenomena so dependent upon each other that one can be expressed as a function of the other, we have an equation. If, now, these same phenomena can be connected by a different equation, and one which could not be reduced to the first equation, it simply means that the phenomena are related in another way. And the discovery of the second relationship in no wise diminishes the significance of the first relationship. Thus Dieterici has shown that the internal heat of vaporization, λ, is equal very approximately to $\mathrm{CRT} \ln \frac{d}{\mathrm{D}}$. This fact in no wise diminishes the importance of the relation

$$\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{\mathrm{D}})$$

pointed out by the author. The one equation arises probably from the motion of the molecules, the other from the attractive forces that operate between them; and since these forces under certain conditions are in equilibrium, it becomes possible to have two different expressions for the same quantity. If Kleeman can show a third true equation for λ, which does not introduce constants or relations having no natural significance, it simply means that there is some third relation existing between the quantities and some "cause" for this relation, and he will have discovered a fact of consequence. The point I wish to stress is that when the equations are really different and really true, they represent different facts.

8. Several years ago * I investigated certain equations obtained on the supposition that the molecular attraction varied as the inverse third, fourth, fifth, and sixth power of

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* Jour. Phys. Chem. xi. p. 156 (1907).

the distance between the molecules. I have in this paper extended the investigation to the inverse seventh power law. It is likewise not in accord with the facts. The inverse second power law gives an equation which is in accord with the facts. This it is impossible to deny. Those who seek to give another interpretation to the equation should remember that all of the other attractive forces follow a similar law as regards their variation with the distance apart of the attracting bodies. It is perfectly true that the numerator factors of these laws now appear to differ. My own idea is that this difference is due to a misconception. I think that the total attraction (molecular, gravitational, electrical or magnetic) could be expressed by the law $f=\frac{\text{constant}}{s^2}$, the constant varying with the nature of the body and the attractive force—perhaps being ultimately identical if its primary origin were understood. I think the usual numerator factors of the attractive force laws, mm' for gravitational, ee' for electrical, etc. deal with the distribution of a perfectly definite attraction.

9. Kleeman further attempts to disprove "Mills' law" by substituting in a formula he has deduced from surface tension considerations [*]. It seems to me that in this particular case Kleeman is trying to make my law conform to his ideas. I am not surprised at its failure to conform to these ideas. I disagree with Kleeman's formulæ and conclusions at many points, as I do here.

Kleeman attempts further to show [†] that the inverse square law of the molecular attraction cannot be true, pointing out the fact long ago recognized, that the gravitational attraction is not great enough to account for molecular cohesion. Sutherland [‡] made the same criticism of the author's point of view. The criticism has already been answered [§]. The molecular attraction obeys the law $f=\frac{\text{constant}}{s^2}$ (or $\frac{\mu M}{s^2}$, if you prefer, where μ is a constant depending upon the nature of the substance, and M is a number identical with or proportional to ordinary mass), and not the law which

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[*] Phil. Mag. Jan. 1911, p. 90.

[†] Phil. Mag. Jan. 1911, p. 89; Aug., p. 356; also vol. xx. p. 902 (1910).

[‡] Phil. Mag. xvii. p. 664 (1909).

[§] Journ. Phys. Chem. xi. pp. 145–153 (1907); xv. p. 417 (1911); Phil. Mag. October 1910, p. 629.

Kleeman is trying to apply, namely, $f=\frac{\mathrm{K\,M\,M'}}{s^2}$, where M and M′ are the masses of the attracting particles.

Prof. D. Tyrer raises an important point * when he says: "We see again that the specific heat of a fluid at constant volume increases as the density increases, and from this it must follow that in an isothermal change in density, intramolecular energy is liberated. This result is of extreme importance in the investigation of the potential energy of liquids and molecular attraction. It vitiates at once all conclusions regarding molecular attraction based on the assumption that during the expansion of a liquid the whole of the energy absorbed goes to do work against molecular attraction, except of course the small amount which does work of expansion against the external pressure." The fact that the specific heat of a gas at constant volume increases as the density increases, and the consequences Prof. Tyrer mentions of this fact, have been long known to me. Never, since my second paper in 1904, have I made the unqualified statement that the total energy of a molecule in the gaseous and in the liquid condition was the same. A distinct statement to the contrary was made in the sixth paper †. Also in a paper on Chemical Energy ‡ attention was called to the fact that there was some energy change which I did not then understand and that the total energy necessary to change a solid monatomic element from −273° C. to the liquid condition at its melting-point was about three times the kinetic energy of translation required by the element at that temperature. I may say that in my opinion it is essentially the fact noted by Prof. Tyrer that makes itself felt in various ways. In attempting to find the true equation of state, and in studying surface tension phenomena, as well as when studying specific heats, I continually found that where *changes of temperature* entered into the phenomena, the relations were not so simple as I had at first supposed. The question was studied from various points of view throughout a period of several years. The true explanation is I think given in my article on Temperature and Molecular Attraction §:

"*The energy given out by any two bodies originally at rest at an infinite distance apart in forming any stable configuration under the action of gravitational attraction is equal to the*

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* Phil. Mag. Jan. 1912, p. 112.

† Jour. Phys. Chem. xi. p. 156 (1907).

‡ Trans. Amer. Electro-chem. Soc xiv. p. 42 (1908).

§ Phil. Mag. July 1911, p. 97.

kinetic energy which they retain and is, for either body, inversely proportional to its mean distance from their common centre of mass." I think unquestionably that a system of n bodies coming together under the influence of the molecular force would behave in so far similarly that *they would retain an amount of energy proportional to that given out.* This amount of retained energy is not to be confused with the kinetic energy of a perfect gaseous condition. The paper cited must be consulted in full. I think it will then be clearly understood, that although the statement of Prof. Tyrer is true, yet in all probability the facts that he mentions are not contradictory of an inverse square law of attraction but are in fact a consequence of that law.

University of South Carolina,
Columbia, S.C., U.S.A.
April 25th, 1912.

XLVI. *Theory of Electric Discharge in a De La Rive's Tube.*

By Prof. D. N. MALLIK, *B.A.*, *Sc.D.*, *F.R.S.E.*[*]

1. WHEN an electric discharge is passed through a De La Rive's tube at different pressures, it is found ("Magnetic Rotation of Electric Discharge," Phil. Mag. Oct. 1908) :—

I. That there are three stages of the discharge : At a high pressure, the discharge is in the form of a shower, consisting of an infinite number of rays. These, gradually,—as the pressure is diminished—form into a single band or stream ; as the pressure is further reduced, the band broadens and ultimately fills the whole tube as a glow discharge.

2. Now an electric discharge is a procession of corpuscles shot off from the negative electrode under the influence of the electric field and ions, positive and negative, produced by collision of these corpuscles with the molecules of the enclosed gas.

The ions and the corpuscles exert electric force on one another, and as they are in motion they exert a magnetic force as well. Moreover, these masses moving through the fluid medium must exert an additional apparent force on one another, besides experiencing a viscous retardation in the direction of motion.

The effect of these forces along a line of discharge affects motion and collision along the line, and therefore need not be considered when we are dealing with the relative influences of different streams.

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[*] Communicated by the Author.

3. Consider now any two (parallel) streams. The resultant action due to electric and magnetic forces due to two charges e, e', moving with equal velocities q, was calculated by J. J. Thomson (Phil. Mag. April 1881), and shown to be a repulsion of magnitude $\frac{ee'}{kr^2}\left(1-\frac{q^2}{3v^2}\right)$, where k is the S.I.C. of the medium, r the distance between the charges, and v, the velocity of light (the moving charges being assumed to be spherical).

Suppose, now, there are n positive and N negative charges in the first stream and n', N$'$ in the second (per unit length of each stream), and q is the velocity of a positive ion, and $-q'$ that of a corpuscle.

Then, the mutual repulsion between the elements ds, ds' will be (if e, e' be the charges of the particles in the two streams)

$$\frac{ee'}{kr^2}ds\,ds'\left[n\,n'\left(1-\frac{q^2}{3v^2}\right)+\mathrm{NN}'\left(1-\frac{q'^2}{3v^2}\right)\right.$$

$$\left.-n\mathrm{N}'\left(1+\frac{qq'}{3v^2}\right)-n'\mathrm{N}\left(1+\frac{qq'}{3v^2}\right)\right]$$

$$=\frac{ee'}{kr^2}ds\,ds'\left[(n'-\mathrm{N}')(n-\mathrm{N})-\frac{(nq+\mathrm{N}q')(n'q+\mathrm{N}'q')}{3v^2}\right].$$

In the case of a discharge, since all the streams are similar, $n=n'$, $\mathrm{N}=\mathrm{N}'$.

$$\text{Therefore the repulsion}=\frac{ee'\,ds\,ds'}{kr^2}\left[(n-\mathrm{N})^2-\frac{(nq+\mathrm{N}q')^2}{3v^2}\right], \quad (1)$$

the ions and corpuscles in any one stream being a self-equilibrating system.

There will be certainly repulsion, therefore, when n is large or small compared with N; for in this case, the expression within square brackets becomes

$$n^2\left(1-\frac{q^2}{3v^2}\right),\ (\mathrm{N}=0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$\mathrm{N}^2\left(1-\frac{q'^2}{3v^2}\right),\ (n=0)\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

while the resultant action will be certainly an attraction if $n=\mathrm{N}$.

4. Next consider the effect of masses moving through the fluid, supposed perfect.

If ρ = density of the fluid, a the radius of a positive ion supposed spherical, and r the distance between them; then it can be shown that the repulsion between them, when moving with velocities q, is

$$\pi\rho \frac{a^6}{r^3} q^2.$$

If, then, there are n positive, N negative charges in either stream per unit length, and b is the radius of a negative sphere and $-q'$ its velocity, the repulsion per unit length of either stream will be

$$\frac{\pi\rho}{r^3}\left[n^2a^6q^2 + \mathrm{N}^2b^6q'^2 - 2n\mathrm{N}\, a^3b^3qq'\right]$$

$$= \frac{\pi\rho}{r^3}(na^3q - \mathrm{N}b^3q')^2 \ldots \quad . \quad . \quad . \quad . \quad (4)$$

That is, the effect is always a repulsion which decreases as the pressure of the gaseous medium decreases. The resultant repulsion per unit length of either stream will, therefore, be equal to the sum of (1) and (4).

On taking account of these two sets of forces, it is easy to see that the observed phenomena must be due to repulsion and attraction between various streams of ions issuing from the various points of the cathode. While, of course, the resultant effect must depend on the relative values of N, n, q, q', the simplest supposition that we can make is that whenever these streams carry mostly one kind of electricity, they will spread all round the tube, but when the streams contain an equal number of both kinds of electrified particles, and the pressure is not too high, the various streams will be attracted together and form a band.

Although it is not possible to trace in detail the change in the value of the above expression, it seems to be possible to follow the course of events in a general manner. Thus, let N_1 = number of corpuscles shot off from the cathode, n_1 = number of ions produced at the anode,

$\mathrm{N}_2 = n_2$ = no. of negative or positive particles produced by collision.

N_3 = no. of corpuscles lost through combination with positive ions or neutral molecules of the gas.

n_3 = no. of positive ions lost through recombination.

Then we may reasonably assume

$$n_3 < N_3,$$

and obviously $$N = N_1 + N_2 - N_3,$$

and $$n = n_1 + n_2 - n_3.$$

5. At a high pressure it is reasonable to suppose that $N_1 > n_1$, and we have (on certain assumptions) experimental evidence for taking $N_2 < N_3$ [see art. 11]. Therefore, so long as this goes on and we may assume $n_2 > n_3$, we have the number of corpuscles tending to equality with the number of positive ions, the former being greater than the latter initially. The expression (1) is on these suppositions positive at first, and since the expression (4) is always positive the resultant effect is one of mutual repulsion of the various streams, producing a spray discharge.

6. When $n = N$, the expression (1) is negative and the total effect will be an attraction when ρ, the density of the gas, is sufficiently reduced. In this event, the various streams agglomerate and continue as a "band" discharge, so long as the resultant action is an attraction.

7. When the pressure is further reduced, the number of collisions must become small, but the number of recombinations may still be sufficient to neutralize the positive ions produced. In the result, we shall have only corpuscles in the tube, and hence the expression (1) will be positive and the resultant action a repulsion, producing a dispersal of the rays [art. 10].

It is, of course, well known that at a very low pressure, a discharge-tube contains only corpuscles. This is further verified by the fact that on the creation of a magnetic field, at low pressure, there is an apparent shortening of the positive column. This is best explained by supposing the corpuscles to move in spirals in the magnetic field, as has been shown by J. J. Thomson that they should (art. 52, &c., 'Conduction of Electricity through Gases'). This is also partially due to the fact that $\frac{\partial Nu}{\partial x} \neq 0$ (eqn. 5, art. 8).

On the whole, then, there will be repulsion between consecutive streams, both at the beginning and at the end, and we have thus three stages of the discharge.

8. II. It is only during the second stage that there is a steady rotation on the application of the magnetic field.

We have already seen that the variation in the number of corpuscles in the discharge at any moment must depend on the number of collisions and recombinations per second. Thus [art. 229, 'Conduction of Electricity through Gases' (2nd edition)] let

λ = mean free path,
X = electric field,
e = charge on an ion.

Then, the mean kinetic energy of an ion $= X\lambda e$.

Now, if $X\lambda e >$ a limiting value P, ionization takes place.

Let $f(X\lambda e)$ = fraction of collisions that result in ionization, i. e. $f(x)=0$, when $x<P$.

Also, let v = average velocity of translation of corpuscles,
N = no. of negative ions per c.c.;

then $\frac{Nv}{\lambda}$ = no. of collisions per second,

and no. of ions produced $= \frac{nv}{\lambda} f(Xe\lambda)$.

Let $\gamma . \frac{Nv}{l}$ = no. of ions that disappear through recombination.

Then $\frac{Nv}{l}[f(Xe\lambda)-\gamma]$ = the resultant no. of ions produced, neglecting those due to positive ions.

Therefore the equation of continuity is

$$\frac{\partial N}{\partial t}+\frac{\partial Nu}{\partial x}=\frac{Nu}{\lambda}[f(Xe\lambda)-\gamma], \quad . \quad . \quad . \quad (5)$$

where u = average velocity of translation due to electric field $= v$ nearly.

Now in order that there should be *steady* rotation of the discharge *as a whole* we must have

$$\frac{\partial N}{\partial t}=0, \quad \frac{\partial Nu}{\partial x}=0 \quad \text{and} \quad \therefore f(Xe\lambda)-\gamma=0.$$

But this is also the condition that the result of collision should be annulled by recombination. We conclude, therefore, that throughout the stage that this condition holds n and N will continue to remain equal, if they are so, as we have argued (art. 6) that they should be, at the beginning.

The quantity γ would obviously depend on the nature of the gas. The same is true of the function f. γ may also depend on the conditions of the experiment—for example, whether the discharge is intermittent or continuous. It may also depend on the pressure.

We shall presently see that we have some information on these points already. Experiments for further elucidating them are in progress.

9. III. In the case of air, the curve connecting pressure and potential difference between the electrodes consists of four portions. The first portion, which is very nearly straight, corresponds to the "spray" discharge. As the "spray" discharge changes into the "band," there is a bend in the curve towards the line of pressure. The next portion is also a straight line. Gradually, the curve bends away from the line of pressure, meeting asymptotically the line of potential difference.

10. We have just seen that $f(\mathrm{X}e\lambda)-\gamma=0$ during the band or rotatory stage, that is $f\left(\frac{\mathrm{X}e}{p}\right)-\gamma=0$, since $\lambda=\frac{1}{p}$, p being the pressure.

If now γ is constant, we have $f\left(\frac{\mathrm{X}}{p}\right)=\text{constant}$, which shows that the curve connecting p and potential difference will in this case be a straight line, if the spark-length is constant (as is known to be the case, both on Paschen's law and experimental grounds).

If γ is not constant, the curve will not be a straight line. This may explain why, in the case of complex gases and vapours, the curve is not a straight line.

11. If $f(\mathrm{X}e\lambda)-\gamma$ is negative, so that $f\left(\frac{\mathrm{X}e}{p}\right)-\gamma=-\alpha$, say, this will correspond to the (first) stage, during which corpuscles are decreasing as the result of collision and recombination and tending to equality with positive ions [art. 5].

Assuming α to be constant and less than γ, we deduce that the curve connecting p and potential difference corresponding to this stage will also be a straight line, inclined at a greater angle to the line of potential difference than the line corresponding to the rotatory stage [art. 10].

This would explain the first bend in the curve [art. 9].

In the third stage of the discharge, the form of the curve is consistent with the supposition that collisions are then few, and $\gamma-\alpha$ rapidly decreases with pressure.

12. It has been found from experiment that hydrogen shows no rotation when the discharge is that due to an induction-coil. This is obviously due to the fact that for such a discharge, $f(\mathrm{X}e\lambda)-\gamma$ is never zero in the case of this gas, or what is the same thing, a steady state of ionization throughout the length of the discharge-tube cannot be established under the conditions of the experiment.

The peculiar behaviour of hydrogen in a vacuum-tube generally would seem to be connected with this property.

That the intermittent nature of the discharge from an induction-coil materially determines the value of $f(Xe\lambda)-\gamma$, is proved by the fact that when the discharge is passed from storage-cells into a tube (of small spark-length), the first stage—that of spray-discharge—is absent.

13. IV. During the rotatory discharge, the product of pressure and angular velocity is constant.

In the case of steady rotation, the moment of the electromagnetic couple on the current due to the magnet is equal to the moment of the retarding forces.

The first is proportional to the current $i=\mu i$ (say), the second $=\int(A_1+A_2)nur\,ds$,

where n=no. of +, − ions per unit length.
r=distance of an ion from the axis and u the velocity
ds=an element of length of the discharge.
A_1, A_2=the retardations of +, − ions per unit velocity.

Also, if q, q' be the velocities of the ions along the line of discharge, and X the electric intensity,

$$Xe=qXA_1 \text{ i. e. } A_1=\frac{e}{q}\text{; similarly, } A_2=\frac{e}{q'}.$$

Therefore $\mu i=\omega ne\left(\frac{1}{q}+\frac{1}{q'}\right)\int r^2\,ds.$

But $$Xe(q+q')n=i;$$

$$\text{therefore } \frac{\omega}{\mu}=\frac{qq'X}{\int r^2 ds}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Now since $$p=\frac{1}{\lambda},\quad p\propto\frac{1}{q}\text{, and also}\propto\frac{1}{q'}.$$

$$\therefore\quad p\omega\propto\frac{X}{p\int r^2 ds}. \quad . \quad . \quad . \quad . \qquad (7) \text{ from } (6).$$

Now $\int r^2\,ds$ is found to be practically constant when the distance between the electrodes remains unchanged,

$$\text{therefore}\quad \frac{X}{p}\infty\, p\omega.$$

But $$f\left(\frac{Xe}{p}\right)=\gamma\text{, so long as there is rotation.}$$

Therefore $f(ep\omega)=\gamma$, i. e. $p\omega=\delta$, say.

If γ is constant, as is practically the case for air, N_2O, &c.

$$p\omega=\text{constant}.$$

If γ is not constant but increases with pressure, $p\omega$ will increase with pressure also.

Comparing this with experimental results, we observe that δ is proportional to molecular weight in either case.

Again, since $\mathrm{V}'=\int \mathrm{X}\,ds$, where V' is the potential difference, if we write $p=a\mathrm{V}'+b$ (for a simple gas during the rotatory stage), a and b will be constants depending on the induction-coil and the nature of the gas.

Substituting in (7), we have (assuming X to be constant along the discharge)

$$p\omega \propto \frac{\mathrm{V}'}{p\int r^2 ds\,.\int ds} \propto \frac{1}{\left(a+\frac{b}{\mathrm{V}'}\right)\int r^2 ds \int ds}.$$

Therefore for any given discharge-tube b is obviously small, since $p\omega=$ constant nearly, as we have just seen, $\int r^2\,ds$ and $\int ds$ being taken to be constant (as we are justified in doing).

We notice, moreover, that since experiment yields the result that $p\omega$ is proportional to the E.M.F. of the induction-coil, a must be proportional to this quantity also.

Finally, if the distance between the electrodes is changed, we have, taking $\int r^2\,ds \propto \int ds = l$, very nearly, where l is the distance between the electrodes, $p\omega l^2=$const., very nearly.

This is also verified by experiment.

XLVII. *Changes in the Dielectric Constant produced by Strain.* *By* E. P. ADAMS, *Professor of Physics, and* C. W. HEAPS, *Experimental Science Fellow, Princeton University*[*].

IN the Philosophical Magazine for December 1911, one of the writers of the present paper showed that the elongation per unit length of a charged thin cylindrical condenser, open at the ends, is given by the expression

$$e=-\left(\frac{\mathrm{V}}{d}\right)^2\frac{(\delta_1+\delta_2)\sigma}{\mathrm{K}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if d, the thickness of the dielectric, is small compared with its internal radius, a. V is the difference of potential to which the condenser is charged, σ Poisson's ratio and K the specific inductive capacity of the dielectric. δ_1 and δ_2 are two constants of the dielectric, supposed isotropic, the former the change in K for unit strain along the lines of force, and the latter for unit strain perpendicular to the lines of force. At the time the former paper was written it was not possible to calculate the amount of the elongation since the values of δ_1 and δ_2 were not known. The object of the present paper is to show how these constants may be measured, and to describe experiments undertaken to determine them for hard rubber and for two kinds of glass.

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[*] Communicated by the Authors.

As shown before *, a series of experiments by Wüllner and Wien on the change in capacity of cylindrical glass condensers when stretched furnish us the means of calculating the combination, $\delta_2-\sigma(\delta_1+\delta_2)$. The expression found for the change in capacity may be written in the form

$$\frac{\delta l}{l}\left\{\delta_2-\sigma(\delta_1+\delta_2)\right\}=\mathrm{K}\left(\frac{\delta \mathrm{C}}{\mathrm{C}}-\frac{\delta l}{l}\right), \quad . \quad . \quad . \quad (2)$$

where l is the unstretched length, and δ_1 the elongation produced by the stretching.

Another relation between δ_1 and δl may be obtained by considering the torsion of a cylindrical condenser. Under a state of torsion, neither the length nor the diameters are changed. The whole change in capacity arises from changes in the dielectric constant. Taking the z axis along the axis of the cylinder the strain components are

$$e_{xx}=e_{yy}=e_{zz}=e_{xy}=0\ ;\ e_{zx}=-\tau y\ ;\ e_{zy}=\tau x,$$

where τ is the angle of twist for a unit length. Using cylindrical coordinates, the only strain coordinate that does not vanish is $e_{\theta z}=\tau r$. We therefore have

$$\delta\mathrm{K}=\tfrac{1}{2}(\delta_1-\delta_2)\tau r=mr.$$

We have to find the capacity of a cylindrical condenser, of internal radius a, external radius b, whose specific inductive capacity is $\mathrm{K}+\delta\mathrm{K}$. If C is the capacity in the unstrained state, and $\mathrm{C}+\delta\mathrm{C}$ in the strained state, we find

$$\mathrm{C}+\delta\mathrm{C}=\frac{\mathrm{K}l}{2\log\dfrac{\mathrm{K}+ma}{\mathrm{K}+mb}\cdot\dfrac{b}{a}},$$

and keeping terms of the first power only in d/a, assuming m to be small,

$$\frac{\delta\mathrm{C}}{\mathrm{C}}=\frac{(\delta_1-\delta_2)\tau a}{2\mathrm{K}}\left(1+\frac{d}{2a}\right). \quad . \quad . \quad . \quad . \quad (3)$$

Therefore measurements of $\delta\mathrm{C}/\mathrm{C}$ for cylindrical condensers

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* Phil. Mag. Dec. 1911, p. 895.

under a state of simple longitudinal tension and also under a state of simple torsion make it possible to determine δ_1 and δ_2 separately.

It is also possible to determine δ_1 and δ_2 for parallel plate condensers. The capacity is: $C=KA/4\pi d$, so that

$$\frac{\delta C}{C}=\frac{\delta A}{A}+\frac{\delta K}{K}-\frac{\delta d}{d}.$$

We shall assume that the armatures are adherent, rectangular in shape, of dimensions a and b.

First, let the condenser be stretched by a tension T applied to the side b, at right angles to the lines of force. We find:

$$\frac{\delta A}{A}=\frac{T}{E}(1-\sigma),$$

$$\frac{\delta d}{d}=-\frac{\sigma T}{E}$$

$$\frac{\delta K}{K}=\frac{T}{EK}\left\{\delta_2-\sigma(\delta_1+\delta_2)\right\},$$

$$\frac{\delta C}{C}=\frac{T}{E}\left[1+\frac{1}{K}\left\{\delta_2-\sigma(\delta_1+\delta_2)\right\}\right],$$

E being Young's modulus.

Next, let the condenser be compressed by a pressure P, along the lines of force, applied to its whole area, the edges being free from traction.

$$\frac{\delta A}{A}=2\frac{P}{E}\sigma,$$

$$\frac{\delta d}{d}=-\frac{P}{E},$$

$$\frac{\delta K}{K}=-\frac{P}{EK}(\delta_1-2\sigma\delta_2),$$

$$\frac{\delta C}{C}=\frac{P}{E}\left\{2\sigma+1-\frac{1}{K}(\delta_1-2\sigma\delta_2)\right\}.$$

As δ_1 and δ_2 enter into these two expressions for $\delta C/C$ in different combinations, they may each be determined.

Experiments with Hard Rubber.

The first experiments were made with hard rubber in the thought that as larger strains could be produced the effects would be larger than with glass. A hard rubber tube, of internal radius 1·78 cm. and wall-thickness 0·1 cm., was coated for a length of 40 cm. inside and outside with a paste made of powdered graphite and thin shellac. Thick shoulders were left at the ends of the tube for convenience in supporting it. For the stretching experiments the tube was supported vertically and weights hung on the lower end. Elongations were read with micrometer-microscopes focussed at two points a fixed distance apart. For the torsion experiments the tube was mounted horizontally in a Wertheim torsion apparatus.

The capacity measurements were made with a Wheatstone's bridge arrangement supplied with current from a Vreeland sine-wave oscillator *, and with a telephone as detector. Two arms of the bridge were nearly equal wire resistances, wound as nearly capacity- and inductance-free as possible. The steady current value of these resistances were 2566·7 and 2569·7 ohms. The hard rubber condenser was placed in the third arm of the bridge. In the fourth arm was a variable air-condenser, and parallel with it, a standard guard-ring air-condenser. In order to secure absolute silence in the telephone it was necessary to put a series resistance in the fourth arm. The conditions for silence are then two:

$$\frac{C}{C_1}=\frac{R_2}{R_1}-\frac{R_4}{R_3}.$$

$$4\pi^2n^2CC_1R_3R_4=1;$$

where R_1 and R_2 are the nearly equal resistances in the first and second arms respectively; C, the capacity of the condenser to be measured, R_3 its resistance; C_1, the whole capacity in the fourth arm, and R_4 the resistance in series in this arm. Since the ratio R_4/R_3 is very small, the first condition reduces to $C/C_1=R_2/R_1$. n is the frequency employed.

The method of making measurements consisted in balancing as nearly as possible with the variable air-condenser, and making the final adjustment with the standard guard-ring condenser. The condenser was then either stretched or twisted, and the known change in capacity of the standard condenser necessary to secure balance gave the change in capacity sought for. The average results obtained for hard rubber follow:—

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* Physical Review, xxvii. p. 286 (1908).

Capacity, $C=1005$ e. s. units.

Length of armatures	40 cm.
Internal radius a	1·78 cm.
Wall thickness d............	0·1 cm.

$$K=3{\cdot}24$$

Stretching weight = 33·6 kg.

$$\delta l/l=1{\cdot}9\ 10^{-3},$$
$$\delta C/C=1{\cdot}4\ 10^{-3},$$
$$E=1{\cdot}7\ 10^{10}.$$

Poisson's ratio was determined by measuring the angle of twist for a known twisting moment M:

$$\mu=\frac{2M}{\pi\tau(b^4-a^4)},$$

$$\sigma=\frac{E}{2\mu}-1.$$

The results were:

$$\mu=7{\cdot}05\ 10^9,$$
$$\sigma=0{\cdot}2.$$

Using (2) we find

$$\delta_2-\sigma(\delta_1+\delta_2)=-0{\cdot}77.$$

When the condenser was twisted no change in its capacity could be detected up to a whole angle of twist of 10° in a length of 44·3 cm. The smallest value of $\delta C/C$ that could be detected was 10^{-3}. By (3) we find that the absolute value of $\delta_1-\delta_2$ is less than 0·09, or we can write

$$c=\delta_1-\delta_2=\pm 0{\cdot}09,$$

as the limiting values of the difference between δ_1 and δ_2. We then find the limiting values of δ_1 and δ_2 separately by combining this result with the value of $\delta_2-\sigma(\delta_1+\delta_2)$ obtained from the stretching experiments:—

c.	δ_1.	δ_2.	$\delta_1+\delta_2$.
+0·09	−1·25	−1·16	−2·41
−0·09	−1·32	−1·41	−2·73
0	−1·28	−1·28	−2·56

Experiments with Glass Condensers.

The only experiments with glass condensers were made with the object of determining a change in capacity when twisted. As no change was found the experiments of Wüllner and Wien enable us to determine the values of δ_1 and δ_2, or at least to find the limiting values between which they must lie.

A silvered glass tube, of internal radius 5 cm., wall-thickness 0·1 cm., and length 55 cm., was twisted through 5°·1 before it broke. The capacity remained constant.

Identifying this kind of glass with Wüllner and Wien's "N.Th.R." we have, from Table I., in the paper referred to :

$$K=8{\cdot}60,$$
$$\sigma=0{\cdot}2,$$
$$\delta_2-\sigma(\delta_1+\delta_2)=-0{\cdot}94.$$

Since the smallest measurable value of $\frac{\delta C}{C}$ was 10^{-3} (3) gives as the limits between which $\delta_1-\delta_2$ lies

$$c=\delta_1-\delta_2=\pm 1{\cdot}06,$$

and we get

c.	δ_1.	δ_2.	$\delta_1+\delta_2$.
+1·06	−0·16	−1·22	−1·38
−1·06	−2·96	−1·90	−4·86
0	−1·57	−1·57	−3·14

Similar results were obtained with a Jena glass tube of length 61 cm., internal radius 1·75 cm., and wall-thickness 0·1 cm. This tube was twisted through 4° before it broke. Identifying this with Wüllner and Wien's No. 10, we have

$$K=6{\cdot}61,$$
$$\sigma=0{\cdot}2,$$
$$\delta_2-\sigma(\delta_1+\delta_2)=-2{\cdot}54,$$

and we find

$$c=\delta_1-\delta_2 \quad =\pm 0{\cdot}62;$$

and we can write:

c.	δ_1.	δ_2.	$\delta_1+\delta_2$.
+0·62	−3·4	−4·0	−7·4
−0·62	−5·0	−4·4	−9·4
0	−4·2	−4·2	−8·4

We can now compare the elongation to be expected on the erroneous theory of electrostriction, *i. e.*

$$e'=\left(\frac{V}{d}\right)^2\frac{K}{8\pi E},$$

with the elongation given by equation (1). Their ratio is

$$\frac{e}{e'}=-\frac{(\delta_1+\delta_2)\sigma}{K}.$$

For soda glass, the kind used by Professor More in his electrostriction experiments, we find

c.	*e/e'.*
+1·06	0·03
−1·06	0·11
0	0·07

Thus the elongation to be looked for is certainly less than 11 per cent. of that which Prof. More expected, and his conclusion that the elongations he obtained were caused by heating is confirmed by these results.

With the Jena glass tube considerably greater elongations can be looked for, as shown by the following table:—

c.	*e/e'.*
+0·62	0·22
−0·62	0·28
0	0·25

It is just possible that using glass tubes of this kind a true elongation caused by electrostriction might be observed.

In conclusion, it appears that one will not go far wrong in taking for solid dielectrics, as for fluid dielectrics, $\delta_1=\delta_2$. Assuming this, the calculation of $\delta_2-\sigma(\delta_1+\delta_2)$ given in the previous paper from Wüllner and Wien's experiments gives at once the values of $\delta_1=\delta_2$ for the kinds of glass which they used.

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XLVIII. *The Maintenance of Forced Oscillations of a New Type.* *By* C. V. Raman, *M.A.*[*]

[Plates X.–XII.]

THE photographs published with this paper (Pls. X.–XII.) represent some of the very remarkable class of maintained oscillations regarding which preliminary communications were published in the issues of 'Nature' dated the 9th Dec., 1909, and the 10th Feb., 1910, under the title of the present paper. I propose here to confine myself to indicating the main features of the phenomena actually observed in experiment, and to elucidating these by the aid of a physical theory that I have since worked out.

One of the most fascinating problems in the dynamics of vibrating bodies is the behaviour of a system when subject to periodic forces which tend merely to alter its "spring" or restitutional coefficient, and do not directly tend to displace the system from its position of equilibrium. In discussing this problem, it is assumed that this periodic change in "spring" is of definite frequency and is imposed from outside the system. One principal point for inquiry is the relation that must exist between this frequency and that of the free oscillations of the system in order that the latter may be permanently maintained in vibration in the presence of dissipative forces. Lord Rayleigh has investigated the particular case in which the frequency of the imposed force is double that of the oscillations of the system, and has shown that under suitable circumstances the oscillation may be maintained. The question arises whether there do not exist other frequency-ratios which would permit of the maintenance of the oscillations of the system. Mr. Andrew Stephenson attacks this problem by pushing to a higher degree of approximation the analytical method employed by Hill in discussing certain problems in the Lunar Theory, and by Lord Rayleigh in working out the particular case of double frequency. His analysis (published in the Quarterly Journal of Pure and Applied Mathematics for June 1906) leads to the result that the oscillations of the system may be magnified or maintained under suitable circumstances, if the frequency N of the imposed variation of spring stands to the frequency N_1 of the oscillation in the relation $2:r$ where r is any positive integer. When r is unity, we evidently have the case of double frequency referred to above.

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[*] Communicated by the Author.

From an acoustical point of view, the possibility of *maintenance* is that which possesses the greatest interest. Mr. Stephenson's treatment is purely mathematical, and his paper does not explain in terms of ordinary physical ideas why it is that the oscillations should admit of being maintained with the specified frequency-relations, nor does he offer any experimental evidence in support of such a proposition. It is necessary therefore to discuss the problem in its physical bearings before any results of experiment can be rendered intelligible.

If the oscillations of the system are to be maintained in the presence of dissipative forces, a continued supply of energy from without into the system is clearly necessary, and we have therefore to show that with the assumed relation between the frequency of the imposed variation of spring and that of the oscillations of the system, it is possible for a finite amount of energy to pass into the system during every complete period of the variation of the spring, and that this is just sufficient to balance the loss by dissipation during the same time. This again would only be possible, if, assuming that an oscillation of any particular frequency was maintained, the product of the imposed variation of spring into the displacement, which may be regarded as the impressed part of the force tending to restore the system to its position of equilibrium, had a periodic component of the same frequency as that of the oscillation proposed to be maintained, and this should also be of a suitable magnitude and phase. This is evident from the general principles of resonance, since components of the restoring force having any other frequency would obviously be comparatively ineffective in maintaining the vibration.

The condition referred to above, it may readily be shown, is satisfied in the case of double frequency. Thus, putting N and N_1 equal to $n/2\pi$ and $n_1/2\pi$ respectively, and assuming that the variation of spring is represented by $-2\alpha n_1^2 \sin nt$ and the displacement ϕ at any instant is equal to $C \cos (nt/2+\epsilon_1)$, it is seen that the product of the variation of spring and the displacement has a periodic component $-\alpha C n_1^2 \sin (nt/2-\epsilon_1)$ which has the same frequency as the oscillation proposed to be maintained. It is readily shown that the work done by this part of the force acting on the system in a time equal to the period of the variation of spring is $\alpha/4 n_1^2 n C^2 t \cos 2\epsilon$, and that this is equal to the loss by dissipation in the same time if $\kappa n = \alpha n_1 \cos 2\epsilon_1$, $2\kappa n_1$ being the dissipation coefficient. This result, it will be seen, is precisely equivalent to that obtained in a different manner by Lord Rayleigh (Scientific Works, vol. ii. p. 192).

Taking now the general case discussed by Stephenson, we may first assume that a motion of frequency $rN/2$ is maintained by the variation of spring $-2\alpha n_1^2 \sin nt$. If ϕ the displacement at any instant is put equal to $C_r \cos (rnt/2+\epsilon_r)$, where C_r is a constant, it is readily seen that the product of the variation of spring and the displacement which may be termed the impressed part of the restoring force is $-2\alpha C_r n_1^2 \sin nt \cos (rnt/2+\epsilon_r)$, and this has obviously no component of frequency $rN/2$ and cannot therefore maintain an oscillation having that frequency. The expression for the work done by it in a time equal to the period of the variable spring will be found equal to zero. The inference is that, if the oscillation is actually maintained, some important term in the expression for the displacement at any instant has been omitted by us to be taken into account. This we now proceed to find directly from physical considerations.

We may, to fix our ideas, consider a case in which the frequency of the oscillations of the system is large compared with the frequency of the imposed variation of spring. It is clear in this case that the successive oscillations of the system are not executed under identical conditions. At one epoch the restitutional coefficient is a maximum, and an oscillation would evidently be executed by the system during this epoch in a shorter time than at the epoch when the spring is a minimum, and the amplitude of the oscillation would also be greater at the latter epoch. The motion of the system in such a case would evidently be similar to that in the atmospheric beats produced by two simple tones one of which has a greater frequency and amplitude than the other (Appendix XIV. of Helmholtz's 'Sensations of Tone'). We have therefore to modify the expression for the displacement applicable in the general case and may assume it to be approximately represented by two terms, one of which has a much larger amplitude than the other and has a frequency in excess of it by that of the imposed variation of spring.

We may therefore put ϕ the displacement equal to

$$C_r \cos(rnt/2+\epsilon_r)+C_{r-2}\cos(\overline{r-2}nt/2+\epsilon_{r-2}).$$

The expression for the restoring force at any instant requires corresponding modification. The product of the variation of spring and the displacement is

$$-2\alpha n_1^2 \sin nt\left[C_r\cos(rnt/2+\epsilon_r)+C_{r-2}\cos(\overline{r-2}nt/2+\epsilon_{r-2})\right].$$

It is readily seen that this has a periodic component of frequency $rN/2$ which is equal to

$$-\alpha n_1^2 C_{r-2}\sin(rnt/2+\epsilon_{r-2}) \text{ if } r>2,$$

or $$-2\alpha n_1^2 C_{r-2}\sin nt\cos\epsilon_{r-2} \text{ if } r=2.$$

The work done by this the "impressed" part of the restoring force during a period of the variation of spring is readily shown to be

$$-\alpha/4rn_1^2nC_rC_{r-2}t\cos(\epsilon_r-\epsilon_{r-2}), \text{ if } r>2$$

or $$-\alpha n_1^2nC_rC_{r-2}t\cos\epsilon_r\cos\epsilon_{r-2}, \text{ if } r=2.$$

The energy dissipated during the same time is

$$\tfrac{1}{4}\kappa n^2n_1\left[r^2C_r^2+(r-2)^2C_{r-2}^2\right]t.$$

Since the 2nd term within the square brackets is the square of a small quantity it may be neglected, and the energy supplied is equal to the energy dissipated if

$$\kappa rnC_r=-\alpha n_1C_{r-2}\cos(\epsilon_r-\epsilon_{r-2})$$

provided $r>2$, or if

$$\kappa rnC_r=-2\alpha n_1C_{r-2}\cos\epsilon_r\cos\epsilon_{r-2} \text{ when } r=2.$$

It is thus seen that the 2nd term in the expression for the displacement is from a physical point of view of very great importance, though its amplitude may be small compared with that of the 1st term which is much the larger part of the oscillation actually maintained. It is not developed or brought out in the final expression for the magnified or maintained motion as given by Stephenson, and the importance of the part played by it in magnifying or maintaining the motion is therefore not made evident in his paper.

It seems well to consider a few numerical examples. If the frequency of the imposed variation of "spring" were 60 per second, the oscillations of the system would be maintained (under suitable circumstances) if the frequency of its free oscillations were nearly equal to 30 or 60 or 90 or 120 or 150 and so on, the degree of approximation to equality necessary increasing as we proceed up the series. The frequency of the maintained oscillation would be exactly 30 or 60 or 90 and so on. But in the case of the oscillation of frequency 60, the motion would be very approximately represented by a periodic term of that frequency plus a small constant. In the case of the 3rd type in the series, the maintained oscillation would be represented by a periodic term of frequency 90 plus a small term of frequency 30. In the 4th case, the motion would be represented by a periodic term of frequency 120 plus a small term of frequency 60 and so on, the 2nd term in each type being less in frequency than the 1st term by 60, which is the frequency of the variation of spring; in the case of the 2nd type in which the frequency of the first term is itself 60, the 2nd term naturally assumes the form of a constant as stated above. The significance of this is that an oscillation when maintained by a variation of spring of the same frequency has for its mean point, not the equilibrium position of the system, but one slightly displaced to one side thereof. This result is no doubt somewhat paradoxical, but there is nothing absurd in it, inasmuch as we are here dealing with motion under variable spring in the presence of dissipative forces. The restoring forces at the points of maximum displacement on either side of the equilibrium position may be equal in magnitude and opposite in sign despite the fact that these displacements from the equilibrium position are themselves slightly different, and a steady oscillation about a displaced mean point is therefore possible. It is readily seen that in this case it is the slight displacement of the mean point of the normal oscillation that enables a surplus of energy to pass from without into the system to counteract the effect of dissipation and thus maintain the motion.

The class of maintained vibrations discussed above can be realized in experiment and caused to yield some very beautiful results that will now be described. The vibrating systems used in the work are stretched strings which seem *prima facie* well adapted for acoustical work on this subject. Important advantages are that their vibrations are visible without any aid, and, secondly, that their frequency can be adjusted with ease and accuracy over a comparatively wide range. With stretched strings again, it is comparatively an easy matter to impose a periodic variation of "spring", *i.e.* of tension in this case, of any desired magnitude and frequency. The experimental arrangements required are fairly simple. A fine string one or two metres in length is taken and one end of it is passed over a peg or a pulley, preferably the former. The other end is attached to the prong of a massive tuning-fork of frequency say 60 or 100 per second, in such a manner that the tension of the string is varied by the motion of the prong. The tuning-fork should be maintained electrically, but for some purposes powerful bowing is sufficient.

It is generally supposed that under these circumstances the equilibrium position of the string becomes unstable and it is thrown into a state of permanent and vigorous vibration only when the frequency of the free oscillations of the string (in its fundamental or other mode) is approximately half of that of the point of attachment. I found that this was not the case. A permanent and vigorous vibration was also maintained when the frequency of the free oscillations of the string was equal to, or one and a half times, or twice, or two and a half times, or thrice that of the fork. This is precisely what is to be expected from the theory dealt with above, and there is absolutely no difficulty in obtaining any one of the first five or six of these types of maintained oscillation each separately by itself, *i.e.* with the frequency of the oscillation of the string having the specified relation to that of the tuning-fork. All that is required is that the tension should be so adjusted till the frequency of the free oscillations of the string in its fundamental mode bears the desired relation to the frequency of the fork. This can be done by trial, and it will then generally be found that the oscillations are maintained.

To obtain the results shown in the photographs (Pls. X.–XII.) a somewhat different procedure is adopted. The vibrating system here dealt with, *i.e.* a stretched string, has not merely one free period of oscillation but a series of such free periods in which it divides up into one, two, or more segments. Since the frequencies of oscillation which a variable spring of given frequency may maintain under suitable circumstances also form a series, it is evidently possible for more than one mode of vibration to be maintained at one and the same time, each with its own appropriate frequency. In other words, the variable spring may maintain a compound vibration, and as the components of this motion need not both or all be in one and the same principal plane of vibration of the string, we may readily obtain by a little calculation and trial types of maintained motion in which the oscillation in one principal plane is of one frequency and in the perpendicular plane of a different frequency. Under these circumstances, the motion of a point on the string in a plane transverse to it is the appropriate Lissajous figure, and the frequency relation between the component motions is thus rendered evident to inspection in a most striking manner.

The photographs represent short sections of the string thus maintained in stationary vibration, one point in the middle of the section being brilliantly illuminated. Fig. 1 shows the ordinary 1st type of maintenance in which the frequency of the motion is half of that of the fork. Fig. 2 shows a compound of the 1st and 2nd types in suitable phase relation, the motion being in a parabolic arc. Fig. 3 is a compound of the 1st and 3rd types. Fig. 4 is a compound of the 2nd and 3rd types which have frequencies respectively equal to and half as much again as that of the fork. Figs. 5 and 6 are complementary, *i.e.* relate to the same type of oscillation, fig. 5 showing one part of the string and fig. 6 another part. In these two photographs, the 1st and 3rd types of maintained motion occur together in one principal plane, and the 2nd type by itself in the perpendicular plane. In fig. 5 the 1st and 3rd types are in similar phases, but in fig. 6 they are opposed, hence the very remarkable split-ring effect in the latter. In fig. 7 we have the 1st and 3rd types again in perpendicular planes, but along with the 3rd type there is a clear addition of the 2nd type as well. Figs. 8 and 9 are complementary, and show the 1st type maintained in one plane, and the 2nd and 4th types together in the perpendicular plane. Fig. 10 shows a compound of the 2nd and 5th types having frequencies respectively equal to and two and a half times that of the fork. Fig. 11 shows the 1st type in one plane and the 2nd and 5th types together in a perpendicular plane. Figs. 12 and 13 are complementary, *i.e.* show different parts of a string under the same conditions. They represent the 1st and 5th types together in one plane and the 2nd by itself in the perpendicular plane. In fig. 12, the 1st and 5th types are in the same phase, and in fig. 13 they are opposed. Figs. 14 and 15 show the 1st type in one plane, and the 2nd and 6th types together in the perpendicular plane. The two latter are in different relative phases in the two photographs.

Regarding the plate as a whole, it is not a little surprising to contemplate that a strictly normal motion imparted to one extremity of a stretched string should result (under suitable circumstances) in such an extraordinary variety of types of oscillation! I do not think I have photographed one-half of the different types that can easily be maintained permanently.

Conclusion :—I have indicated some of the principal results of experimental interest obtained with this class of maintained vibrations. Further experimental work on the leading types and a detailed comparison with the results of the physical theory which I have outlined above and with the mathematical analysis, does not fall within the limits of the present paper, and I hope to deal with them on an early date. Meanwhile I must remark that the existence and physical importance of the small "second" term of lower frequency in the expression for the maintained motion is directly demonstrable by stroboscopic observation of each of the five or six types of maintained motion referred to above and by a study of their "vibration-curves." The results of this work are being prepared for publication. The experiments and observations recorded in this note were made at the Physical Laboratory of the Indian Association for the Cultivation of Science, Calcutta.

XLIX. *On the Relative Intensities of the Earth's Penetrating Radiation on Land and Sea. By* Professor J. C. McLennan, *University of Toronto* [*].

I. *Introduction.*

SINCE the discovery of the existence of a penetrating radiation at the surface of the earth in 1902 [†], numerous measurements of its intensity have been made in different localities by different observers using a variety of measuring instruments.

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[*] Communicated by the Author. Read before the Royal Society of Canada, May 17, 1912.

[†] McLennan & Burton, Phil. Mag. v. 1903; Cooke, Phil. Mag. vi. 1903.

In these measurements the intensity of the radiation was generally found by determining the ionization produced by it in the air confined in a metallic receiver. In some of these determinations care was taken to have the metallic receiver air-tight, but in a number of them this precaution was not taken, either through its being considered unnecessary or for other reasons.

From the results of these measurements it would appear:—

(1) That the soil and rocks of the earth contribute by far the greater proportion of the radiation.

(2) That the intensity of the radiation is less over such bodies of water as Lake Ontario, the Swiss Lakes, the Southern Atlantic, and the Indian Ocean, than it is over land lying contiguous to these waters.

(3) That the intensity of the radiation when measured at different levels above the ground in the neighbourhood of Braunschweig *, and on such structures as the Eiffel Tower † and the City Hall Tower ‡ at Toronto, decreases with the altitude of the point of observation, but when measured from the basket of a gas-balloon at a height of over 1000 metres above Vienna §, is practically the same as it is at the surface of the earth in that locality.

(4) That in some localities marked daily variations occur in the intensity of the penetrating radiation, while in others no indications of such variations have been found.

(5) That the ionization produced in the air in metallic receivers by the penetrating radiation together with the rays from the walls of the vessel, and by other unknown contributory agents, varies according to different observers from 3·5 to over 30 ions per c.c. per second.

From this summary it will be seen that there is a marked lack of agreement in regard to (i.) the diminution of intensity with altitude, and (ii.) the daily variations in intensity. Two questions still open are:—Is there a diminution in the intensity of the penetrating radiation with increasing altitude or not, and are the periodic variations in the ionization noted by some observers due to variations in the intensity of

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* Bergwitz, *Habilit-Schrift Braunschweig*, 1910.

† Wulf, *Phys. Zeit.* xi. p. 811 (1910).

‡ McLennan & Macallum, Phil. Mag., Oct. 1911.

§ Hess, *Phys. Zeit.* xii. p. 998 (1911).

the penetrating radiation, or are they due to other influences which have not been eliminated in the conditions of measurement?

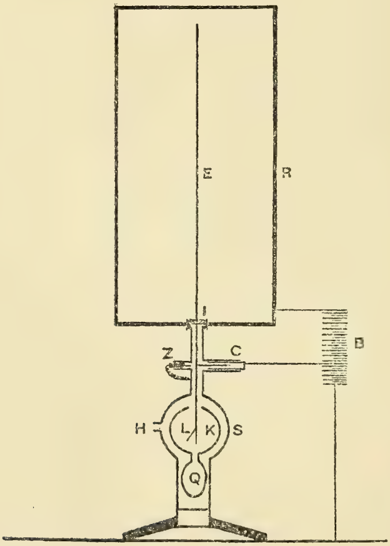
One of the best ways of answering these questions would be for the same observer with the same instrument to make measurements at points for which we have results which do not agree, and measurements such as those recently made by Simpson and Wright * on the 'Terra Nova' and at all points of call on their voyage to the South Pole, which are of that character, will do much to clear up some of the obscure outstanding points in connexion with the anomalous results at present on record.

II. *Observations on the Penetrating Radiation in Different Localities.*

Some measurements made by the writer during a recent stay in Great Britain, and during the voyage following to Canada, also throw some light on one of the questions raised above.

In these measurements the arrangement of apparatus used was the one adopted by the writer and by Wright † and Cline ‡ on different occasions at Toronto. It is shown in fig. 1. The measuring apparatus was the well-known

Fig. 1.



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* Simpson & Wright, Proc. Roy. Soc. Ser. A, vol. lxxxv. p. 175 (1911).

† Wright, Phil. Mag. xvii. 1909.

‡ Cline, Phys. Rev. xxx. 1910.

C. T. R. Wilson compensating condenser gold-leaf electrometer. The receiver R, which had a capacity of about 30 litres, was made of a sample of zinc about ·5 mm. in thickness, which on comparison with a number of different samples was found to contain the least amount of radioactive impurities. The electrode E was provided with an earthed guard-tube at I where it entered the receiver, and the ionization in the receiver was measured by applying saturating voltages to the latter by a battery of dry cells connected as shown in the figure.

Extreme care was taken before commencing the measurements to have the receiver R hermetically sealed so that there could be no possibility of air containing active emanations entering it during the course of the observations. A small aneroid barometer was supported inside the receiver with its face directly in front of a glass window sealed into the wall of the vessel, and tests made with it from time to time showed that the sealing remained secure and intact throughout all the measurements.

In making these tests the receiver was carried from a cool room either to a warm one or out into the bright sunshine. This procedure was always followed by a rise in the barometric reading owing to the air in the vessel becoming heated. While the receiver was kept in the warmer position the high reading was always steadily maintained, but on taking it back to the cooler place the reading just as regularly rapidly fell to its former value. This behaviour showed that no air escaped from the receiver during the period when the pressure was greater than that of the atmosphere outside.

A summary of the results obtained in these measurements at a number of points of observation is given in Table I. (p. 524).

The final readings given in the table are the means of a number taken at each observation point. Those at Cambridge were made in a small brick cottage, the property of the Cambridge Scientific Instrument Co., and the thanks of the writer are due to the Manager, Mr. R. S. Whipple, for placing this building at his disposal and for very kindly assisting in taking practically all of the readings in that place.

Those at Bowland were taken in a room in the residence of Mr. William Ramsay, a large stone structure, while those in the Meteorological Observatory, a stone building, were made with the kind permission of the Director, Mr. R. F. Stupart. The Physical Laboratory at Toronto, in which one of the sets of readings was made, is constructed of brick.

From inquiries it was learned that in none of these four observing stations was there any radioactive contamination by reason of the introduction of radium or other radioactive substance.

TABLE I.

Observation Point.	"*q*." The number of ions produced in the receiver per c.c. per second.
1. Cambridge, England	9·03
2. Bowland, Midlothian, Scotland	8·32
3. The Physical Laboratory, Toronto	9·08
4. The Meteorological Observatory, Toronto	8·88
5. The Lawn of the Meteorological Observatory, Toronto.	6·74
6. The Atlantic Ocean, on s.s. 'Grampian,' sailing *ex* Glasgow, Sept. 16, 1911.	
Sept. 17 ...... 6·42	
18 ...... 6·51	
19 ...... 5·97	
20 ...... 5·42	
21 ...... 6·58	
22 ...... 5·66	
23 ...... 5·78	
24 ...... 5·92	
Mean 6·03	6·03

From the numbers given in the table it is evident, in the first place, that the value obtained for "*q*" was practically the same when the point of observation was taken inside either a brick or a stone structure at points so far separated from each other as Cambridge, England, Bowland, Scotland, and Toronto, Canada.

In the second place, from the measurements made at the Meteorological Observatory, Toronto, it is clear that the building itself contributes in a measure to the penetrating radiation, for the readings obtained on the lawn near that building were on the average more than 1 ion per c.c. per second less than those taken inside the observatory.

In the third place, the numbers show that all the values obtained for "*q*" on the s.s. 'Grampian' were less than any of those obtained on land.

Further, the mean of these readings, 6·03 ions per c.c. per sec., agrees well with the reading obtained by Simpson and Wright[*], 6·3 ions per c.c. per sec., on the 'Terra Nova' on the open sea. Moreover, as the value found for "q" over the water of Toronto Bay with a receiver of the same material as the one used in this investigation was 4·4 [*] ions per c.c. per sec., and as Simpson and Wright obtained 4·1 per c.c. per sec. for "q" on a small skiff on the open sea, it would appear that the effective radiation from a large ship such as the 'Grampian' is practically the same as that from a vessel of the size of the 'Terra Nova' [†].

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[*] Simpson & Wright, Proc. Roy. Soc. Ser. A, vol. lxxxv. p. 175 (1911).

A point of interest in connexion with the readings taken on the steamer (which, however, may possibly be purely accidental) is the gradual drop which they show after leaving Glasgow until Sept. 21st was reached. The reading opposite this date is the mean of those taken during the day preceding the passage through the Straits of Belle Isle. It is higher, it will be seen, than any of those taken during the voyage. The reading 5·78 ions per c.c. per sec. was taken when in the River St. Lawrence near Rimouski, and the last, 5·92 ions per c.c. per sec., as the steamer was approaching Quebec. The numbers it will be seen show a gradual rise during the passage up the river.

III. *On Variations in the Intensity of the Penetrating Radiation.*

Although the time at the disposal of the writer in making the observations was limited, and as a consequence they were not as extensive as one would wish to have them, still they were sufficiently numerous at two stations in Great Britain to show that if variations did occur at these two places, such variations in the intensity were not greater than at most two or three per cent., which is about the accuracy with which readings can be made with the instrument used.

The successive readings taken at Cambridge on a number of different days are given in Table II., and those taken at different times at Bowland, Scotland, are given in Table III.

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[*] *Loc. cit.*

[†] [*Note added June* 30, 1912.] In some measurements made by the writer in collaboration with Mr. A. R. McLeod since the presentation of this paper in May, with the receiver used in the experiments described above, a value was obtained for "q" of 4·46 ions per c.c. per sec. over the waters of Lake Ontario. In this case the observation station was a small platform supported by four long gas-pipes driven into the sand at a point in the Lake where the water was four metres deep. It is interesting to note that the value is practically the same as that obtained by Wright and the writer in 1909 on the ice over the waters of Toronto Bay.

TABLE II.

Values of "*q*" obtained at Cambridge.

Date.	Hour of the day.	Value of *q*.
Aug. 17 ……	3.30 P.M.	9·22 ions per c.c. per sec.
18 ……	5.30 P.M.	9·52
21 ……	6.00 P.M.	8·84
25 ……	6.45 P.M.	8·76
28 ……	5.30 P.M.	8·82
Sept. 1 ……	12 noon	8·98
2 ……	10.45 A.M.	9·19
4 ……	10.50 A.M.	9·00
5 ……	10.30 A.M.	8·95
		Mean 9·03

TABLE III.

Values of "*q*" obtained at Bowland, Scotland.

Date.	Hour of the day.	Value of *q*.
Sept. 14……	10 A.M.	8·32 ions per c.c. per sec.
	11 A.M.	8·32
	12 noon	8·32
	1 P.M.	8·32
	2.30 P.M.	8·32
		Mean 8·32

The readings given in Table II. it will be seen, with the exception of that obtained on August 18th, vary by not more than 3 per cent. from their mean value, while those given in Table III. were the same, namely, 8·32 ions per c.c. per sec. for measurements made between 10 o'clock in the morning and half past two in the afternoon, the rate of movement of the gold leaf in all five of these observations being constant. In so far as these observations go, therefore, it seems certain that variations in the intensity of the penetrating radiation at the observation stations selected at Cambridge and in Scotland do not exist in amount greater than 2 or at most 3 per cent.

This result is in practical agreement with what had previously been found to characterize the radiation at Toronto, and this characteristic, taken in conjunction with the low value found for "q" over the waters of Lake Ontario, is what led the writer to conclude that the soil of the earth and not its atmosphere nor any of the celestial bodies was the chief source of the penetrating radiation.

In conclusion, I wish to acknowledge my indebtedness to my assistants Mr. P. Blackman and Miss A. T. Reed, for making some of the reductions and for taking a number of the readings at Toronto.

Physical Laboratory, University of Toronto.
May 1, 1912.

L. *Further Experiments on Delta Rays.*
By NORMAN CAMPBELL, *Sc.D.*[*]

1. IN three recent papers[†] the problem of the velocity of the delta rays and its dependence on the velocity of the exciting alpha ray and the material from which they are emitted has been discussed. At the end of the last paper it was pointed out that most of the phenomena which had been observed could be reconciled with the view that the delta rays possessed no finite initial velocity greater than a small fraction of a volt and that this view, if it could be accepted, would simplify greatly the theory of ionization. The general method of experiment had been to determine the relation of the current flowing between two plates, from which delta rays were being emitted, to the potential difference between those plates, and there was some evidence that this relation was determined as much by the energy required to drag the slowest rays away from the place where they originated as by the energy required to prevent the fastest rays leaving that place.

But all observers agree that delta rays can leave a plate struck by alpha rays, even when that plate is at a positive potential of some volts with regard to its surroundings. The rays must, therefore, be leaving the plate with a finite velocity, and if, as has been suggested, this velocity is not conferred on them in the act of emission, some source of energy competent to confer it after they have been emitted must be found. When the suggestion was put forward, it appeared that such a source of energy might be found in a process analogous to voltaic action, for the acquirement of a spontaneous positive charge by a body struck by alpha rays had never been observed except when the electrodes were of different materials. The first of the miscellaneous experiments here described was designed to test this hypothesis.

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[*] Communicated by the Author.

[†] Phil. Mag. Aug. 1911, p. 276; Jan. 1912, p. 46; April 1912, p. 462.

2. There is one remarkable feature which distinguishes radioactivity and its effects in ionization from almost all other processes: they are independent of the temperature. If the relation of the current to the potential difference were determined by secondary causes unconnected with radioactivity and ionization, then that relation should change with the temperature; but if it is determined by the primary causes of emission of the delta rays, then it should be independent of the temperature.

The experiment was made by insulating about 1 mm. apart two parallel copper plates, one of which was covered with polonium, in an evacuated glass vessel. The vessel was strongly heated during exhaustion to drive off air from the solid contents. The relation of the current to the potential difference between the plates was then determined (1) at room temperature, (2) when the vessel was heated to the softening point of the glass, (3) when the vessel was immersed in liquid air. Not the smallest difference could be detected between the relations for (1) and (3); in (2) all the currents were about 3 per cent. greater than in (1), a difference which could be attributed to the fact that gas had not been completely eliminated from the vessel, or possibly to the beginnings of thermionic emission. It may be safely concluded that the emission of delta rays is independent of the temperature, and that the velocity of those rays is determined by processes directly connected with the action of alpha rays on the atoms they strike. It is necessary to imagine that the rays really start with an initial velocity of some volts.

3. Definite evidence that the form of the relation between current and potential difference was influenced by the effect of the field in dragging delta rays out of the electrodes had been produced only in the case when one of the electrodes was covered with soot. It appeared that if this action was important, the relation ought to be determined by the electric field between the plates rather than by the potential difference between them. Experiments were accordingly made with the apparatus described in the last of the three papers to discover whether the relation was changed when the distance between the electrodes (and, therefore, the field for a

given potential difference) was changed. The electrodes were covered with aluminium, and the distance between them could be altered in the ratio of 1 to 2·5 (approx.) without violating the necessary geometrical conditions. The following table shows that the relation between current and potential difference is independent of the field strength, and that, when the electrodes are of aluminium, the form of the relation is determined by the velocity of the rays. It is not proved that, in this case, the "simple theory" of that relation, given in the first paper, is adequate, for the possibility of a reflexion of the rays, which depends upon the velocity, has to be taken into account Nevertheless, these two experiments do much to remove the uncertainties which were previously attached to interpretations of the experiments based on that theory; it appears that some small proportion of the rays, at least, must have an initial velocity as great as 10 volts.

TABLE I.

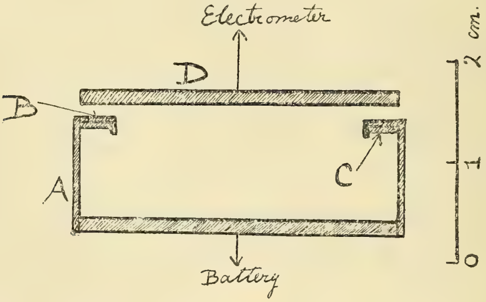
P.D.	Current.	
	Electrodes ·05 cm. apart.	Electrodes ·12 cm. apart.
10	1·000	1·000
9	·987	·985
8	·968	·968
7	·948	·950
6	·926	·927
5	·889	·889
4	·839	·837
3	·755	·759
2	·634	·643
1	·412	·423
0	0	0

4. It was concluded from the previous work that the relation between current and potential difference, and therefore the distribution of the initial velocities of the rays, was independent of the velocity of the exciting alpha rays. The velocity of the exciting rays had been varied only by inserting absorbing layers in the path of the rays from polonium. A variation over a wider range was now obtained by substituting for the polonium the active deposit of thorium obtained from a preparation of mesothorium. The range of the polonium rays is 3·9 cm., that of the rays from ThB and ThD 5·0 and 8·6 cm. The experiments

mentioned in the last paragraph and many others have been repeated with the substitution of the thorium deposit for polonium ; in no case has any alteration due to the substitution been detected. It may be taken as quite certain that the velocity of the delta rays is perfectly independent of that of the alpha rays by which they are excited.

5. Many of the difficulties in interpreting the results of the experiments described in the first two papers arose from the fact that in all cases the rays proceeded from both of the electrodes between which the current was measured. It was difficult to decide whether the effect of an increase in the potential of one electrode was due to a stopping of the rays proceeding from that electrode or to an increase in the number proceeding from the other. It appeared that, if only an apparatus could be obtained in which the rays proceeded from one electrode only, then it would be possible to determine accurately the maximum speed of the rays at least, for it would be that corresponding to the positive potential on that electrode which is sufficient to prevent any current passing. At length the apparatus shown in fig. 1 was designed and seemed to fulfil the necessary conditions.

Fig. 1.



The active material, which in this case was the active deposit of thorium, is deposited on the under side of the ring C. The alpha rays from it can excite delta rays at the interior surface of the box A, and these rays can emerge through the hole in the top of the box and reach the other electrode D ; but the alpha rays cannot strike any other part of the apparatus, so that there is no other source of delta rays. Both electrodes were, of course, contained in a vessel which could be exhausted.

Preliminary experiments showed that, if the hole in the top of A were covered with the thinnest possible aluminium foil, no detectable current could be made to pass between the electrodes. It was clear that the desired conditions were attained, in that all delta rays were produced within A and that no disturbance was introduced by the β and γ rays emitted by the active deposit.

6. If there were no air in the vessel and if none of the delta rays were reflected at the electrode, the relation of the current to the potential difference between A and D would give directly the distribution of the velocities of the rays. When the potential difference is zero, all the rays emerging through the hole strike D; when the potential of A is V above that of D, all the delta rays having an initial velocity less than V will be prevented from reaching D. Accordingly, if i_V is the current flowing to D corresponding to the potential V, i_V/i_0 should be the proportion of the rays having a velocity greater than V. When V is very great i_V should be zero, and it should be zero also for all values of V when a magnetic field of sufficient strength is established in a direction parallel to the surface of D, so as to prevent any of the rays from A reaching D. The values of the current when V is negative do not concern us; they merely indicate how many electrons can be dragged from inside A by an external field.

Fig. 2.
A & D both Aluminium.

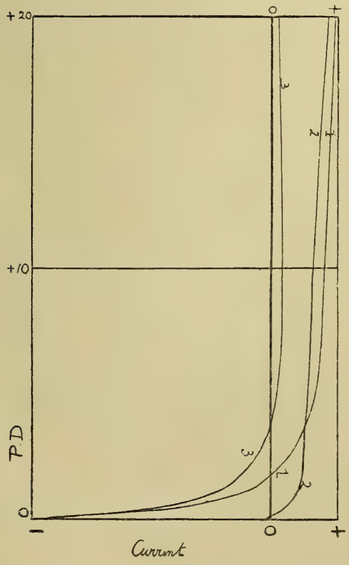
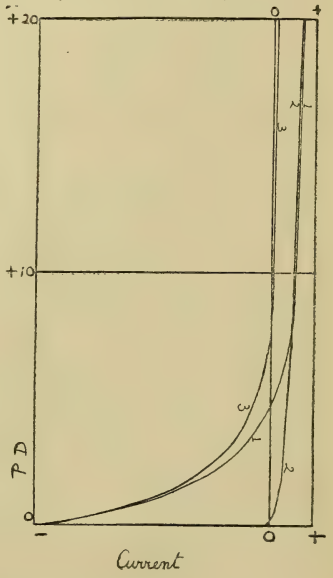


Fig. 3.
A, Aluminium; D, Soot.



Figs. 2 and 3 show the nature of the curves determined experimentally. In fig. 2 both A and D were of aluminium;

in fig. 3 A was of aluminium while D was covered with soot; in each case curve 1 represents the readings without a magnetic field, 2 with a magnetic field, and 3 the difference between 1 and 2. The magnetic field was of such a strength that a further increase in it produced no further effect. A correction is made in every case for the activity of the thorium deposit, so that the readings are comparable.

7. It will be noted that in the curves 1 the current for large values of V is not zero, but a finite positive quantity. The existence of a positive current would seem at first sight necessarily to indicate that positive ions were travelling from A to D, for the preliminary experiments with the hole covered with aluminium leaf show that no delta rays are liberated from D. These ions are naturally attributed to the presence of gas remaining in the vessel, but their number is unexpectedly large. Observations with the vessel containing gas at measurable pressures showed that the current due to the presence of air at the pressure indicated by the McLeod gauge should be only 0·1 per cent. of the current carried by the delta rays, whereas it appears to be some 15 per cent. It is probable that some of the gas adhering to the surface of A is only liberated when the alpha rays strike it and ionize it; a similar explanation of some of his observations has been put forward by Pound in a recent paper,* and it is doubtless correct. But if the positive current is due to this cause, it should be unaffected by the action of a magnetic field; for experiments at higher pressures showed that such a field had no influence on the current due to the ionization of the air, at least for potential differences greater than 2 volts. In fig. 3, when D was covered by soot, the application of a magnetic field does not change the magnitude of the positive current, but when D is of aluminium the magnetic field decreases the positive as well as the negative current. Similar measurements, when D was of brass and gold, showed that it was only when D was covered with soot that the positive current was unchanged by the magnetic field, and it was also noted that in this case the positive current was somewhat smaller than the others.

8. There seems only one explanation possible of the change of the positive current with the magnetic field. In his work on the reflexion of slow electrons, v. Baeyer † has shown that electrons with speeds of the order of 10 volts excite so many secondary rays at the surface of metals on which they are incident, that it is possible for more electrons to leave such

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* V. E. Pound, Phil. Mag. May 1912, p. 813.

† O. v. Baeyer, *Phys. Zeit.* x. p. 176 (1909).

a surface than fall upon it. If a fast delta ray which can travel against a potential difference of 10 volts excites at D more than one secondary ray, then there will obviously be a positive current to D which will be stopped when the delta rays are prevented from reaching D by the application of a magnetic field. And since v. Baeyer found that soot shows practically no reflexion, the difference which has been noted between soot and metals is immediately clear.

In a similar manner it may be possible to explain a curious phenomenon which, though it was suspected in the previous experiments, was not mentioned for lack of certainty. It now appears that it has also been observed by Pound (*loc. cit.*) and there can be no further question as to its reality. In such measurements as were described in the first two papers, especially when the electrodes were covered with aluminium, it was found that an increase in the potential difference between the electrodes beyond the 16 volts necessary to attain saturation to 40 or even 100 volts produced a small but noticeable decrease in the current[*]. The only explanation I can offer of this decrease is that a delta ray from the negative electrode sometimes attains a sufficient speed in travelling through the 16 volts to enable it to liberate a secondary ray which can travel back to the negative electrode against the field; such an action presents no difficulty on the score of energy, for the rays start from the negative electrode with a finite speed. The number of such secondary rays liberated would increase with the potential difference between the electrodes so long as the power of exciting secondary rays increased with increase in the velocity; v. Baeyer has shown that a stage is reached later when the power of exciting secondary rays decreases with increase in velocity; but I have never been able to observe in the cases mentioned a second increase of the current with the potential difference.

9. If the explanation offered is correct, it is clear that the form of the curves will be materially influenced by the reflexion of the delta rays at the electrode D, unless this electrode is covered with soot. In all other cases the quantity i_V/i_0 will not represent accurately the proportion of the rays which have a velocity greater than V, for the number retained by D will depend, not only on the number of rays striking it, but also on the number reflected from it. But unless A is also covered with soot, we introduce another source of error in covering D with soot rather than with the same material

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[*] See, *e.g.*, Table 2, column 1 (page 534).

as A; there will be a Volta difference of potential between the electrodes, and the actual P.D. will not be that read on the voltmeter.

It is possible that a way out of this dilemma might be found by the use of some of the methods described recently by Compton * in his work on the influence of the Volta effect on the measurement of the speed of the photoelectric electrons. But even those methods were not completely successful, and the results which have been already attained appear to me so conclusive that a further elaboration of the apparatus would not be justified. In any case, it would be very difficult to obtain extremely accurate measurements, for in the neighbourhood of V=0 the current changes so rapidly with V and with the geometrical form of A, that the exact reproduction of a curve is almost impossible. The apparatus is also extremely sensitive to small magnetic fields; if a piece of soft iron of 30 c.c. volume is placed near the electrode the current for V=0 is changed about 5 per cent. It is certain that the earth's magnetic field has some influence on the shape of the curves. The quantity i_{10} was taken as standard, because saturation appears to be attained with about 10 volts, so that $i_0 - i_{10}$ represents the whole current, and $i_0 - i_V$ that part of it carried by rays of which the speed is less than V. Since only comparative values are important the choice of a standard is unimportant.

10. The results of the measurements are given in Table II.

Table II.

P.D.	Current.							
	D same as A.				D covered with Soot.			
	Al.	Brass.	Au.	Soot.	Al.	Brass.	Au.	Soot.
20	·996	1·000	1·002	1·016	1·023	1·015	1·010	1·016
10	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
9	·998	·997	1·000	·994	·995	·990	·995	·994
8	·997	·993	·999	·987	·988	·981	·990	·987
7	·996	·988	·995	·972	·980	·975	·986	·972
6	·993	·984	·991	·958	·962	·960	·974	·958
5	·980	·970	·975	·932	·928	·933	·954	·932
4	·959	·957	·932	·907	·883	·906	·913	·907
3	·925	·894	·873	·844	·819	·830	·855	·844
2	·856	·832	·777	·727	·679	·753	·750	·727
1	·710	?	·535	·509	·437	?	·510	·509
0	0	0	0	0	0	0	0	0

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* Compton, Phil. Mag. April 1912, p. 579.

The unit of P.D is 1·035 volts, and the quantities termed "current" are the values of $\frac{i_0-i_V}{i_0-i_{10}}$ for curves obtained, like those marked 3 in figs. 2 and 3, by substracting the values of the current with the magnet on from those with the magnet off; thus they are corrected for the presence of residual air. It will be seen that it is quite impossible to say precisely for what P.D. saturation is attained. The curves when D is covered with soot appear to require a higher potential for saturation than the others, but I am sure that the apparent saturation in the latter case is due to the influence of reflexion which has already been noted; it will be observed that in one case the current for V=20 is smaller than for V=10. The uncertainty attaching to any single measurement of current does not exceed ·005, but it was found that, owing to the causes just mentioned, readings could not be reproduced with this accuracy when the apparatus had been taken down and put up again.

The influence of reflexion at the electrode D in the first half of the table and that of the Volta effect in the second half make it unlikely that, even if the distribution of speed among the delta rays from different substances were the same, all the numbers in the same row of the table would be the same. But it will be seen that there is a very general agreement between the figures for different metals, and such divergencies as there are in one half of the table are not reproduced in the other. The figures for gold in the first half are less than those for aluminium, in the second half they are greater. I have no hesitation in ascribing these divergencies to the influence of reflexion of the Volta effect and of unavoidable small changes in the apparatus, and I have no hope of producing more satisfactory evidence that *there is no material difference in the quality of the delta rays emitted by different substances.* It is true that the differences between the various materials is greater here than in the experiments described in the first two papers, which were not regarded as conclusive as to the identity of the rays, but the sources of error are now definitely known, whereas before it was uncertain whether the measurements gave any information at all as to the speed of the delta rays.

11. Accepting this conclusion some further questions require consideration.

Bumstead[*] has suggested that the delta rays are emitted from an air film on the surface of the materials and not from the materials themselves, so that it is only natural that they should appear always of the same quality. It seems to me sufficient evidence against this view that different materials obviously reflect the rays differently: if the rays can penetrate the air film (from which doubtless *some* rays come) when they are incident on the material, surely some of the rays excited in the material must be able to emerge. It is just possible, however, that the differences which have been observed with different materials are caused only by a difference in the state of the air film on their surfaces. But I have never found that the most drastic treatment for removing air films has produced any considerable change in the form of the curve.

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[*] Bumstead, Phil. Mag. Dec. 1911, p. 907.

Secondly, we may ask, What is the velocity of the delta rays? I think it is clear from these experiments that there is no definite velocity and that rays are emitted with widely different speeds ; some, probably about half of them, seem to have a velocity of less than 1 volt, while others seem to have speeds as great as 10 or 20 volts. It is to be remembered that the rays are emitted at all angles with the surfaces of the electrode, whereas it is only the component of their velocity perpendicular to the electrodes which is effective in carrying them across. But this fact is not sufficient to account for the apparent heterogeneity of the rays. It is easy to show that if the rays were emitted with the same speed of V_0 volts, but in all directions, we should have (when V lies between 0 and V_0)

$$\frac{i_0 - i_V}{i_0} = \left(\frac{V}{V_0}\right)^{\frac{1}{2}}.$$

The curve should touch the axis of potential at $V=0$, and should have a marked " knee " at the point where saturation is attained; the actual curves exhibit neither of these features.

On the other hand, heterogeneity of the rays may possibly be due to a loss of velocity by those rays which are not produced actually in the surface in passing through the intervening layer. Since the rays are completely stopped by the thinnest material layers obtainable, it seems impossible to test this hypothesis.

12. Some further experiments have been made with the apparatus described in the paper on " Ionization by Alpha Rays " (*loc. cit.*) on the current through a layer of gas at low pressure contained between parallel electrodes and ionized by alpha rays. The electrodes were covered with aluminium ; in one series they were about $\frac{1}{2}$ mm. apart, in

another about $1\frac{1}{2}$ mm.; the results given below apply equally to both series.

In the former experiments measurements were never made with a potential difference less than that required to saturate the delta ray current when the vessel was completely exhausted. Accordingly the variations of current noted can never have been due to any effect of the field in stopping the delta rays from one electrode from reaching the other. It appeared that it might be possible to obtain some information as to the delta rays liberated in the gas, and not at the electrodes, by measurements with much smaller potential differences.

Let us suppose that the delta rays are liberated uniformly throughout the gas by the alpha rays, that they are all projected from the atoms with the same velocity of V_0 volts, but that their velocities are equally distributed in all directions; let us suppose further that the pressure of the gas is so low that very few encounters occur between the delta rays and the molecules, and that the positive ions have initial velocities so low that they all travel to the negative electrode under the smallest potential differences with which we are concerned. Then a simple calculation will show that, if N delta rays and N positive ions are liberated per second in the gas, the relation between V and the current i will be

$$i = \epsilon N\left(\frac{1}{2} + \frac{1}{3}\sqrt{\frac{V}{V_0}}\right)$$

if V is less than V_0,

$$i = \epsilon N\left(1 - \frac{1}{6}\frac{V_0}{V}\right)$$

if V is greater than V_0.

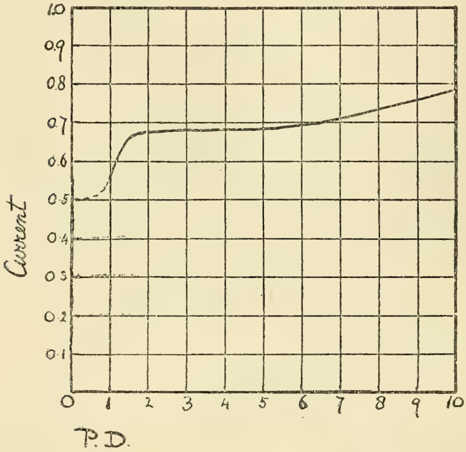
It is to be noted that the tangents to the two portions of the curve are coincident at the point where they cut, so that the curve has no "knee," but if the relation between i and V turned out to be that predicted an estimate of the value of V_0 could be obtained.

13. If collisions between the delta rays and the molecules occurred, this theory would not be applicable. It was thought that, if the current for all P.D.'s was found to be proportional to the pressure of the gas (and therefore to N) for all pressures under a certain limit, it might be assumed that the effects of such collisions were negligible. However, in the experiments on air it was found that the current for all P.D.'s between 1 and 15 volts was accurately proportional to the pressure, until a pressure of 4 mm. was reached with the smaller

distance between the electrodes, or a pressure of 1·5 with the larger. At the highest of these pressures collisions between the rays and the molecules must have been frequent, for (1) calculation shows that the mean free path of the electrons is not large compared with the distance between the electrodes, and (2) when P.D.'s of some 50 volts were employed, unmistakable signs of ionization by collisions appeared. It is clear, therefore, that the measurements cannot be expected to conform to the theory given, but, though no explanation of them can be given as yet, they seem of sufficient interest to be mentioned.

In fig. 4 the relation is plotted between the P.D. and the current expressed as a fraction of that which would be carried

Fig. 4.



by all the ions liberated by the alpha rays, i. e. ϵN. The value of N was extrapolated from that found at higher pressures, when a true saturation current could be obtained and was found to be accurately proportional to the pressure. The effect of the delta rays from the electrodes was eliminated in all cases by substracting from the current at any given pressure that obtained with the same P.D. when the pressure was zero.

It will be seen that the curve is curiously like that obtained with much higher pressures and higher P.D.'s, where saturation is obtained over a certain range of P.D.'s and the current subsequently increases as ionization by collision enters. But the "saturation" which is obtained in this case occurs when only about 0·7 of the ions produced reach the electrodes.

14. When hydrogen was substituted for air, still more strange results were obtained. In this case, the current proved not to be proportional to the pressure for any finite range at low pressures. The addition of a very small quantity of gas to the previously exhausted vessel did not increase the current at all; in some cases it appears even to decrease it. But the most remarkable feature occurred when the relation between the current and the P.D. was examined for these low pressures. In Table III., column 1 gives the relation for a pressure of 1·1 mm. and a distance between the electrodes of about 1½ mm., column 2 gives the relation for a pressure zero, and column 3, which is the difference between 1 and 2, the relation for the part of the current which would be expected to be due to the gas only. It will be observed that for a certain range of low potentials the current seems to decrease with an increase of potential. No explanation is offered at present of this result, which is typical of those obtained with hydrogen, or of the results with air; they are recorded merely in order to show that there are many things connected with conduction through ionized gases which still wait to be explained.

TABLE III.

P.D.	Current.		
	1.	2.	3.
50	1201	711	490
30	1043	713	330
20	937	713	224
10	812	699	113
8	771	684	87
6	720	652	68
5	592	633	59
4	654	598	56
3	596	545	51
2	516	465	51
1	399	325	74
0	0	0	0

Summary and Conclusions.

2–4. It is shown that, in the case of a current carried by delta rays from metals, the relation between the current and the P.D. is independent of the temperature of the electrodes; also that the current is determined rather by the P.D. between the electrodes than by the electric field in the space between them. It is concluded that the delta rays must be emitted originally with a finite velocity and that the velocity which they have been found to possess is not due, as was suggested in a former paper, to secondary causes.

5–11. Experiments with a new form of apparatus have proved to the satisfaction of the author that there is no difference in the velocities of delta rays emitted from different materials. The conclusion formerly announced that these velocities are also independent of the velocity of the exciting alpha ray receives much more complete confirmation. Evidence is quoted against the view that the delta rays from all materials appear to be the same, because they come from a layer of air on the surface of those materials and not from the materials themselves.

The same experiments show that the delta rays are very heterogeneous in velocity; most of them appear to have velocities less than 3 volts, but a very few may have velocities as high as 10 or 20 volts. It is possible, but not probable, that this heterogeneity is imposed on originally homogeneous rays by passage through the surface layers of the material from which they come.

11–13. The results of some measurements on the currents through air and hydrogen at low pressures and under low P.D.'s are quoted. They exhibit remarkable features of which no explanation is offered.

If the conclusions of this paper are accepted, the ivestigation enters on a new phase. If the delta rays are emitted with velocities which depend neither on the nature of the material from which they come nor on the velocity of the rays which excite them, on what do those velocities depend? It seems that either we must imagine that they depend on some structure common to all materials, or on the nature of the helium atom of which all alpha rays consist. Some decision between the alternatives may be obtained by examining the process of ionization by agents other than alpha rays. Several recent investigators have spoken of the "delta rays liberated by Röntgen rays," but there appears to be no experimental evidence whether the electrons ejected from atoms by these agents possess finite velocities at all similar to those possessed by the electrons liberated by alpha rays. Endeavours will now be made to obtain such experimental evidence.

The University of Leeds,
May 1912.

Note added Aug. 22.—Experiments which will be described in the next number of the Phil. Mag. show that Röntgen rays liberated delta rays precisely similar to those liberated by alpha rays.

LI. *On Bridge Methods for Resistance Measurements of High Precision in Platinum Thermometry.* *By* F. E. Smith, *A.R.C.Sc.**

(From the National Physical Laboratory.)

THE object of this communication is to describe certain new bridge methods of measuring with high precision the resistance of a platinum thermometer, or similar resistance.

The desirability of investigating the resistance-measuring apparatus of platinum thermometers was first brought to the author's notice by a communication made by Dr. Chree † to the Royal Society. Afterwards Dr. J. A. Harker described sundry troubles met with in precision work, and tests made by ourselves on several resistance bridges for thermometric measurements indicated that many of the difficulties pointed out by Dr. Chree still remained. The present important position of platinum thermometry in standardising-laboratories was a further incentive to this research.

The accuracy aimed at in high precision platinum thermometry is very considerable. At low temperatures, a measurement within 0°·001 C. is not regarded as an extravagant aim, while at higher temperatures, such as 800° C., the temperatures are usually recorded within 0°·01 C. Between 0° and 100° C. a difference of temperature of 0°·001 corresponds to a change in the resistance of the thermometer of nearly 4 parts in one million, and at 800° C. a change of temperature of 0°·01 C. corresponds to a resistance change of about 10 parts in a million.

Dr. Chree in the paper already referred to suggested certain improvements in apparatus to reduce the possible sources of error in platinum thermometry. Dr. Chree used a Callendar-Griffiths' bridge, the resistance coils of which were of platinum silver, and for accurate work it was necessary to know the temperature of the coils within less than 0°·1 C. He suggested as an alternative to this that the resistances should be made of some material with a small temperature coefficient of resistance. Happily, this is now the case in all modern resistance bridges, manganin being the material in common use.

Dr. Chree suggested also that the uncertainties arising out of the plug-contact resistances should, if possible, be reduced, or the resistance of the platinum thermometer increased. The difficulty of securing a sufficiently constant plug-contact resistance is very great, and because of this, plugs have, in many cases, been abandoned in favour of mercury contacts. This is so in many of the Callendar-Griffiths bridges made by the Cambridge Scientific Instrument Co., and mercury contacts could be used in the bridge employed by Professor Callendar in 1902. It is satisfactory to know that the mercury contacts fulfil the requirement with respect to constancy.

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* Communicated by Dr. R. T. Glazebrook, C.B., F.R.S.

† Chree, Proc. Roy. Soc. vol. lxvii. (1900).

Of the other improvements suggested by Dr. Chree, three related to the resistance bridge and one to the current used in the measurements. These are as follows :—

1. It is desirable that some simple and more perfect method should be devised for eliminating the effects of changes in the relative resistance of the leads and the proportional arms.
2. The bridge-wire scale is too much contracted for very exact work with thermometers of such low resistance as the ordinary Kew ones; it is desirable, if accuracy to $0^{\circ}\cdot001$ C. is aimed at, that 1 cm. of bridge wire should not answer to more than $0^{\circ}\cdot1$ C.
3. If possible the causes of wanderings in the bridge centre and of thermoelectric currents—not eliminated by the Griffiths key—should be removed.
4. Unless the heating effect of the current can be exactly ascertained and allowed for, the sensitiveness of the galvanometer should be largely increased, so as to render unnecessary, currents whose heating effects will sensibly influence the readings.

We are not aware of any such improvements in the resistance-measuring apparatus having been made, nor do we know of any experiments on the effects of changes in the compensating leads, other than those described in Dr. Chree's paper.

It was the changes in the relative resistance of the leads that was the principal cause of the apparent changes in the zeros of the platinum thermometers during Dr. Chree's investigation. In one instance, the change in the leads in less than one month was equivalent to $0^{\circ}\cdot05$ C., and at the end of that time there was a sudden alteration equivalent to $0^{\circ}\cdot12$ C. As these changes have been fully discussed by Dr. Chree it is unnecessary to go into details here. However, we thought it possible that the leads now in use might be much superior to those employed at Kew 12 years ago, and so we made further experiments which are now described.

Compensating Leads.

Three pairs of leads were examined. One pair, which had been in use for five years, was obtained from Dr. Harker of the Thermometric Department of the Laboratory, and two new pairs were kindly lent to us by The Cambridge Scientific Instrument Co.

The leads obtained from Dr. Harker were of the usual plaited flexible type, and were about 4 yards long. The C leads had a resistance of about 0·06 ohm, and the P leads were nominally equal in resistance to them. Resistance measurements with an accuracy within 1 part in 10,000 showed that the resistance of the leads altered if they were much disturbed. The ratio C/P was first measured as 1·0060, but we found during the first few minutes of our work that the ratio was far from constant.

In order to measure the changes with accuracy, the C and P leads were connected so as to form two arms of a Wheatstone bridge, the other arms of which consisted of two 1-ohm coils of manganin, which could be shunted to secure a balance. The contacts were carefully made, and the terminals and parts of the leads near thereto were guarded against strain. The values of the ratio C/P given in the first columns of Tables I. to III. were obtained when the leads were stretched nearly to their full extent. When the leads were still stretched but considerably agitated before making the measurements the ratios in the second columns were obtained, while those in the third columns relate to observations made with the leads in the form of coils. There does not appear to be any relation between the ratios and the disposition of the leads. The ratios for any one pair of leads were all measured on one day.

TABLE I.

Leads from Dr. J. A. Harker.
Resistance of C leads=about 0·060 ohm.
„ „ P „ = „ 0·060 „
Ratio C/P :—

1·0059	1·0049	1·0050
82	43	77
99	50	42
46	58	
44	67	
	51	
	58	

Maximum variation=0·57 per cent.

TABLE II.

Leads A from the Camb. Scientific Inst. Co.

Resistance of C leads = about 0·112 ohm.
" " P " = " 0·112 "
Ratio C/P :—

1·0014	1·0006	0·9997
0·9997	1·0003	0·9999
1·0005	1·0006	0·9999
0·9999	0·9999	1·0006
1·0000	0·9999	0·9999
0·9999	0·9995	0·9986
0·9997	0·9992	0·9995

Maximum variation = 0·28 per cent.

TABLE III.

Leads B. from the Camb. Scientific Inst. Co.

Resistance of C leads = about 0·112 ohm.
" " P " = " 0·113 "
Ratio C/P :—

0·9865	0·9853	0·9859
0·9867	0·9846	0·9870
0·9857	0·9857	0·9848

Maximum variation = 0·24 per cent.

The changes which we have recorded might conceivably have taken place during measurements of temperature. If the leads obtained from Dr. Harker were used with a platinum thermometer of 2·6 ohms resistance at 0° C., a *change* of 1 per cent. in the ratio C/P would introduce an error of 0°·06 in measurements of temperature. During our observations the ratio changed by 0·57 per cent., which is equivalent to about 0°·034 C. The change of 0·28 per cent. recorded for the A leads (Table II.) corresponds to about 0°·031 C. These errors are very considerable, although not so large as those recorded by Dr. Chree. For measurements accurate to 0°·001 C. the ratio of C to P must keep constant within 1 part in 10,000 if the C leads have a resistance of 0·1 ohm.

The changes in the ratios are, we think, easy to explain.

When Professor Mather and the author made experiments with the Ayrton-Jones current balance [*], it was found that some fine-stranded flexible leads (quite new) were not constant in their resistance because of the comparatively large number of places at which the strands were broken. The difficulty was overcome by replacing the leads by others of less flexibility and containing strands of copper 0·38 mm. in diameter.

As a practical way of eliminating the changes in the relative resistance of thermometer leads, we suggest the abolition of leads of fine strands of wire, and the substitution of leads, preferably short, each of one conducting wire of copper. The leads should be strengthened near the ends so as to fix strong terminals to them, and the four leads might be bound together so as to ensure all being at practically the same mean temperature.

In putting forward this suggestion we are aware that the importance of keeping the compensating leads low in resistance and as invariable as possible has not been overlooked by all workers in platinum thermometry, but nevertheless it is still the common practice, even in precision work, to use flexible leads of the type we have experimented with. The abolition of such leads cannot fail to lead to greater accuracy in temperature measurements and to add to the already great utility of the Callendar-Griffiths bridge.

The Heating Effect of the Current.

Passing now to the heating effect of the measuring current. That the resistance of a platinum thermometer is increased by an appreciable amount when the usual measuring current is passed through it was recognized in the earliest days of platinum thermometry. In 1887 Professor Callendar [†] estimated that his thermometers increased in temperature by 0°·016 C. when a current of 0·01 ampere passed through them. In 1899 [‡] Dr. Chree pointed out that the heating effect due to a given number of watts expended in the wire was not the same at all temperatures, there being a diminution in the heating effect as the temperature rises. It was necessary to point this out as some observers at that time proposed to keep the watts constant at all temperatures.

In 1902 [§] Prof. Callendar made a very complete statement on the heating effect. In his paper on "Continuous Electrical Calorimetry" he states "the cooling effect of conduction and convection currents of air in the thermometer tube increases nearly in proportion to the absolute temperature. The effect of radiation also becomes important at high temperatures, and the cooling is then more rapid. If, therefore, the watts are kept constant, the heating effect will diminish as the temperature rises, and a small systematic error will be produced. Assuming that the rate of cooling increases as the absolute temperature θ, and that the watts are kept constant, the heating effect at any temperature θ is $273\,h/\theta$, where h is the heating effect in degrees of temperature at 0° C." Prof. Callendar states that a better rule is to keep the *current* through the thermometer constant, as in this case the heating effect also is nearly constant if the current flows sufficiently long for the heating effect to be steady.

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[*] Ayrton, Mather & Smith, Phil. Trans. A. ccxxiv. p. 523 (1908).

[†] Callendar, Phil. Trans. A. clxxviii. p. 184 (1887).

[‡] Chree, Proc. Roy. Soc. vol. lxvii. (1900).

[§] Callendar, Phil. Trans. A. cxcix. p. 55 (1902).

Recently, Waidner and Burgess * have measured the heating effect of the measuring current on a thermometer of 1·34 ohms fundamental interval, and found the increments of temperature at 0° and 100° C. to be 1°·65 and 1°·69 respectively when a current of 0·1 ampere was used. At the sulphur point the increase of temperature for the same current was 1°·20 C.

While we believe it is now the general practice to keep the current constant, as suggested by Prof. Callendar, we thought it would be of interest to make fairly accurate observations with a thermometer of 1 ohm fundamental interval. The results which follow show that in our experiments, with a current of 0·1 ampere, the corrections for the increases of temperature at the ice and steam points are practically the same as those observed by Waidner and Burgess, but at the sulphur point the correction for the rise of temperature is about 0°·65 C. greater. In all cases the diameter of the platinum wire was 0·15 mm. In measurements of the highest precision it appears to us to be necessary to determine the corrections for increments of temperature for various currents, at temperatures over the range through which it is proposed to work.

To measure the current we placed two sensitive and similar ammeters in the P and C arms of a Callendar-Griffiths bridge, and thus directly measured the current through the platinum thermometer. The results at 0°, 100°, and at the sulphur point are given in the following tables. The corrections given in the last columns of the tables are those to be applied for the heating effect *in all four arms of the bridge.* The current values are correct within less than 1 per cent.

* C. W. Waidner & Burgess, Bull. Bur. of Stands. vol. vi. no. 2 (1910).

TABLE IV.

Observations at the ice point. Thermometer K 5.

i (amperes).	i^2.	Bridge wire reading =b.w.r.	$\Delta i^2 = (i^2 - 0{\cdot}00023)$.	$\Delta t = \Delta$ b.w.r. =(b.w.r. − 5·758).	Calculated correction $= i^2 \times 162$.
0·015	0·00023	5·758	......	......	0°·037 C.
0·020	0·00040	5·786	0·00017	0·028	0·065
0·039	0·00152	5·970	0·00129	0·212	0·246
0·040	0·00160	5·980	0·00137	0·222	0·259
0·050	0·00250	6·125	0·00227	0·367	0·405
0·060	0·00360	6·300	0·00337	0·542	0·583
0·011	0·00012	5·735	0·00348*	0·565*	0·019

$\Sigma\Delta t/\Sigma\Delta i^2 = 1{\cdot}936/0{\cdot}01195 = 162$, *i. e.* at about 0° C. 0·1 ampere would necessitate the application of a correction of 1°·62 C.

* These values are $(0{\cdot}00360 - i^2)$ and (6·300 − b.w.r.) respectively.

One hour afterwards the following results were obtained when the thermometer was at the steam point.

TABLE V.

Observations at the steam point. Thermometer K 5.

i (amperes).	i^2.	b.w.r.	$\Delta i^2 = (i^2 - 0{\cdot}0001)$.	$\Delta t = \Delta$ b.w.r. =(b.w.r. − 6·315).	Calculated correction $= i^2 \times 168$.
0·010	0·0001	6·315	......	......	0°·017 C.
0·020	0·0004	6·365	0·0003	0·050	0·067
0·030	0·0009	6·446	0·0008	0·131	0·151
0·040	0·0016	6·570	0·0015	0·255	0·269
0·050	0·0025	6·721	0·0024	0·406	0·420
0·060	0·0036	6·902	0·0035	0·587	0·605
0·010	0·0001	6·312	0·0035†	0·590†	0·017

$\Sigma\Delta t/\Sigma\Delta i^2 = 2{\cdot}019/0{\cdot}0120 = 168$, *i. e.* at about 100° C. 0·1 ampere would necessitate the application of a correction of 1°·68 C.

† These values are $(0{\cdot}0036 - i^2)$ and (6·902 − b.w.r.) respectively.

At the sulphur point the results were as follows :—

Table VI.

Observations at the sulphur point. Thermometer K 5.

i (amperes).	i^2.	b.w.r.	$\Delta i^2 = (i^2 - 0{\cdot}0001)$.	$\Delta t = \Delta$ b.w.r. $=$(b.w.r.$-9{\cdot}19$).	Calculated correction $= i^2 \times 185$.
0·010	0·0001	9·19	......	......	$0^{\circ}{\cdot}01_9$
0·020	0·0004	9·25	0·0003	0·06	$0{\cdot}07_4$
0·030	0·0009	9·34	0·0008	0·15	$0{\cdot}16_7$
0·040	0·0016	9·46	0·0015	0·27	$0{\cdot}29_6$
0·050	0·0025	9·64	0·0024	0·45	$0{\cdot}46_3$
0·060	0·0036	9·84	0·0035	0·65	$0{\cdot}66_6$
0·010	0·0001	9·20	0·0035*	0·64*	$0{\cdot}01_9$

$\Sigma\Delta t/\Sigma\Delta i^2 = 2{\cdot}22/0{\cdot}0120 = 1{\cdot}85$, *i. e.* at the sulphur point 0·1 ampere would necessitate the application of a correction of 1°·85 C.

* These values are $(0{\cdot}0036 - i^2)$ and ($9{\cdot}84 -$b.w.r.) respectively.

Summarising the results of Tables IV. to VI. we have for this particular thermometer and bridge, corrections to the temperature readings of 1°·62, 1°·68, and 1°·85 C., at temperatures in the neighbourhood of 0°, 100°, and 445° respectively for a measuring current of 0·1 ampere ; and corrections of 0°·016, 0°·017, and 0°·019 for the usual current, viz., 0·01 ampere, employed in precise work. The corrections at 0° and 100° may be taken as identical with the value 0°·016 given by Prof. Callendar in 1902 for the same type of thermometer, and his suggestion to keep the current and not the watts constant, at all temperatures, is evidently the one for general adoption. If this rule be followed, an adjustment of an external resistance is in general necessary as the temperature changes. Thus in the usual Callendar-Griffiths bridge with 5-ohm ratio coils, a 1 ohm fundamental interval thermometer, and an applied E.M.F. of 2 volts from a storage-cell, the external resistance at 0° C. would be about 133 ohms, and at 100° C. 118 ohms to maintain a constant current of 0·01 ampere through the thermometer. However, if the resistance was not varied a maximum error of 0°·004 only would result over the range 0° to 100°.

At this point it is well to call attention to the bridge described on pp. 557, 558. In this, the resistance of all four arms of the bridge keep constant whatever the temperature of the thermometer may be, and no change of external resistance is necessary. In precision work accidental errors are thus avoided *.

It is now of interest to calculate the minimum time during which the current must flow through the thermometer before the heating effect can be said to be sufficiently steady for an observation of resistance to be made.

The wire of the thermometer with which we experimented was 49 cm. long and 0·0152 cm. (0·006 inch) in diameter. If R is the resistance of the wire, L its length, r its radius, and θ a small difference of temperature between the wire and its surroundings due to a current i, then h the thermal emissivity of the surface is given by

$$h=0{\cdot}038\, i^2\mathrm{R}/\theta \mathrm{L}r,$$

from which we have calculated the following values of h at the ice point, the steam point, and the sulphur point :

h.†	Temperature.
0·0016	0°
0·0021	100°
0·0037	445°

If the maximum increase of temperature due to the current is θ_1 and θ is the increase of temperature t seconds after completing the circuit, then

$$\log_e \theta_1 - \log_e (\theta_1 - \theta) = 2ht/\Delta rs,$$

where Δ is the density of the platinum wire, and s is its specific heat. Using this equation we have calculated for 0° C. the increments of temperature for various values

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* A constant current method was first introduced by Professor Callendar in 1891. In this method the platinum thermometer is connected on the compensator side of the box in series with the box coils, and is balanced against a compensated resistance, equal to, or greater than, the resistance of the thermometer at the highest point of the range it is desired to cover. Phil. Trans. A. vol. ccxii. p. 19 (1912).

† These values are calculated on the assumption that the thermometer increases in temperature by 0°·016, 0°·017, and 0°·019 at 0°, 100°, and 445° respectively, due to a current of 0·01 ampere (see Tables IV. to VI.).

of t, the current being 0·01 ampere. The results are as follows :—

$\Delta = 21{\cdot}5$ $\quad s = 0{\cdot}032$ $\quad r = 0{\cdot}0076$.

t.	θ_1.	$\theta_1 - \theta$.	θ.
1 second	$0^\circ{\cdot}016_5$	0·0089	$0{\cdot}007_6$
2 seconds		0·0048	$0{\cdot}011_7$
3 ,,		0·0027	$0{\cdot}013_8$
4 ,,		0·0014	$0{\cdot}015_1$
5 ,,		0·0007	$0{\cdot}015_8$
6 ,,		0·0004	$0{\cdot}016_1$
7 ,,		0·0002	$0{\cdot}016_3$

For this particular thermometer it is seen to be necessary to keep the circuit closed for from 6 to 7 seconds at least, when precise measurements are being made with a current of 0·01 ampere. For larger currents a longer interval is necessary.

Heating Effect in the Bridge Arms.

In most resistance bridges, three of the arms are of some kind of resistance alloy, and the fourth arm (containing the resistance to be measured) is of some other material. If the temperature of the bridge arms is varied there is in general a disturbance of the balance owing to the temperature coefficient of resistance of the material in three of the arms being different to that of the material in the fourth arm. To overcome this difficulty a compensated bridge was patented by Prof. Callendar in 1887, but it has not come into general use. In the case of a bridge it is obviously better to consider the increments of *resistance* than the increments of temperature due to a given current.

With regard to the limiting value of the current it is well known that the sensitiveness of any method for comparing two resistances is proportional to the current employed in making a measurement, and hence a lower limiting value is fixed by the sensibility of the galvanometer. The upper limiting condition is that none of the arms of the bridge shall change appreciably in resistance owing to the increase of temperature produced by the current, or that the changes shall be capable of accurate estimation.

We now consider the heating effect of a current through two substances of different specific resistances placed in series. When a current i is passed through a straight wire so as to produce a small increase of temperature θ and the temperature of the wire has become steady, the increase of resistance per ohm of the wire is given by

$$0{\cdot}038\, i^2\rho\alpha/hr^3,$$

where ρ is the specific resistance of the conductor, α the temperature coefficient of resistance, h the thermal emissivity of the surface, and r the radius. If we at first choose two wires of different materials but of equal radii, then since h is practically the same for both wires, we have for the same current

$$\text{Increase of Resistance per Ohm} \propto \rho\,\alpha.$$

It is probable that manganin has the smallest value of $\rho\alpha$ of any well-known conductor. The value varies considerably, but taking a mean value as unity, the values for certain metals are approximately as follows:—

Silver	10
Copper	10
Platinum	80
Mercury	800

Thus the current which causes a manganin wire to increase in resistance by 1 part in 100,000 will bring about an increase in the resistance of a wire of platinum of equal radius of about 80 parts in 100,000. This is on the supposition that the cooling media are similar. If, however, the manganin is in well-stirred oil and the platinum wire is in air, the rate of cooling in the first case may be from 20 to 100 times that in the latter, and the percentage increase of resistance of the platinum wire may be 1600 times or more that of the manganin. It is clear that if the diameter of the platinum is less than that of the manganin, the percentage increase of resistance will be still further increased *.

When the manganin wire is covered with silk and shellack, and wound so as to form the usual kind of resistance-coil, the effective cooling surface is, of course, appreciably reduced, but it will readily be seen that comparatively high resistance-coils of manganin of fine wire, immersed in oil, may be placed in series with the usual low resistance B.A. form of platinum thermometer or equivalent

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* In a liquid cooling agent, possibly also in air, h varies as $r^{-1/2}$.

resistance, without any reduction of sensitiveness due to a smaller upper limiting value for the current *.

In Methods 3 and 4 described in this paper, high resistance-coils of manganin are so placed in series with a platinum thermometer, but these do not decrease the sensitiveness of the bridge (in fact they slightly increase the sensitiveness), and the increase of resistance of these coils due to the current passing through them is, in general, negligible.

To remove the possibility of any appreciable error being introduced due to the heating effect throughout the bridge, and to simplify the labour of calculation, it is best to experimentally determine the correction to be applied to a thermometer reading in the way that has been done in Tables IV. to VI. The corrections given in the last columns of these tables do *not* give the temperature rise of the thermometer due to the current, but the correction to the thermometer-reading for the heating in all four arms of the bridge. However, in the experiments cited, the heating of the manganin coils was so small that the corrections are practically equal to the temperature rise of the thermometer. The observations on which the corrections are based occupied about 30 minutes for each of the fixed points.

We would further suggest that the coils of a thermometer bridge be immersed in well-stirred paraffin oil kept at a constant temperature, as such a procedure considerably increases the precision of the measurements. When *standardising* the bridge the resistance of the coils should be calculated for an infinitely small measuring current.

Resistance Measuring Apparatus.

We now proceed to describe in detail several new methods for measuring the resistance of a platinum thermometer, all of which practically eliminate the effects of small changes in the relative resistance of the leads, and have, we believe, several advantages over methods hitherto used.

In the most refined work in platinum thermometry measurements are made within $0^{\text{C}}\cdot001$ C., and we have, therefore, adopted this as a standard by which methods of measurement may be compared. Also we have designed the resistance-bridges so that thermometers with current and potential leads may be used, as these admit of the detection with certainty of secular changes in the resistance of the platinum spiral or "bulb."

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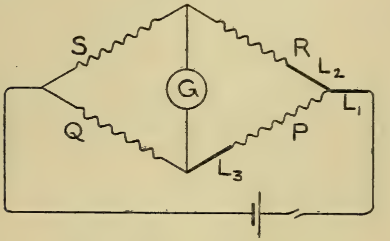
* In 1893 Prof. Callendar employed platinum silver coils in series with a platinum thermometer, the resistance and dimensions of the coils being chosen so that the percentage increase of resistance of the platinum thermometer due to the current was practically equal to the percentage increase of resistance of the platinum silver. Phil. Trans. A. cxcix. p. 55 (1902).

When measurements of the highest precision are to be made we believe that Method 2 will be found most convenient, but for calorimetric work, where rapid balancing is often desired, the dial resistance-bridges (Methods 3 and 4) should be extremely useful. In many such measurements readings accurate within 0°·01 C. are ample, and then the accuracy with which the bridge coils need to be adjusted is considerably less than that indicated in the text.

The resistance of a platinum thermometer is most frequently measured by means of a Callendar-Griffiths bridge *. When the Siemens bridge † (fig. 1) is employed, the thermometer has three leads L_1, L_2, and L_3. Q and S are the ratio-coils and R is the adjustable resistance which is nominally equal to P. If $Q=S$ and $L_2=L_3$, then balance is obtained when

Fig. 1.



$$R=P.$$

The leads are then completely compensated for as in a Callendar-Griffiths bridge, but there is an important difference which is often overlooked. In the Callendar-Griffiths bridge a slide wire joins the thermometer arm with the adjustable resistance, but in the Siemens bridge it is impossible to use a slide wire if the ratio Q/S is to be kept constant.

A third form of platinum thermometer has two current and two potential leads. Previously the resistance of such a thermometer has been measured in two ways: (1) by the potentiometer, and (2) by the Kohlrausch method of overlapping shunts, a differential galvanometer being employed. We now describe several bridge methods for measuring the resistance of such a thermometer.

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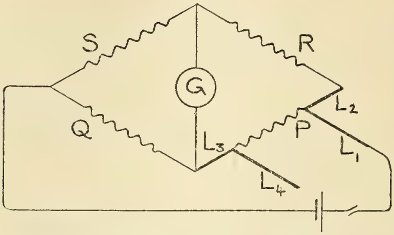
* Callendar, Phil. Trans. A. clxxviii. p. 184 (1887).

† W. Siemens, Proc. Roy. Soc. vol. xix. p. 351 (1871).

First Method.

The resistance scheme is that of a simple Wheatstone bridge, as will be seen from the connexions shown in fig. 2.

Fig. 2.



P is the platinum thermometer with current leads L_1 and L_4 and potential leads L_2 and L_3. Q and S are the ratio arms and R is the adjustable resistance. There will be no current through the galvanometer when

$$P+L_3=Q(R+L_2)/S \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When this balance has been made the potential lead L_2 is disconnected from R and joined to Q ; L_3 is joined to R and the battery lead is disconnected from L_1 and joined to L_4. The new balancing condition is

$$P+L_2=Q(R'+L_3)/S, \quad . \quad . \quad . \quad . \quad (2)$$

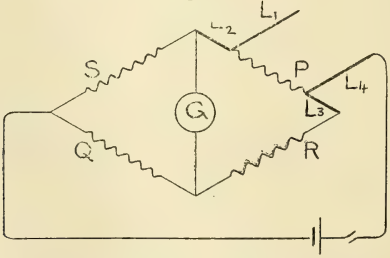
R' being the new value of R. From (1) and (2) we have

$$2P=Q(R+R')/S+(L_2+L_3)(Q/S-1) \quad . \quad . \quad (3)$$

If $Q/S=1$, then $P=(R+R')/2$.

However, it is not well to impose on a bridge the condition that the ratio coils shall be exactly equal. If we suppose that Q/S is equal to $(1+\alpha)$ where α is small, a slightly different procedure must be adopted. At the same time as the leads L_1 and L_4 are reversed in position, the arms P and R are interchanged * (fig. 3).

Fig. 3.



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* If P and R are interchanged in position instead of Q and S, any current through the galvanometer due to a thermal E.M.F. in P is unchanged in direction.

If this is done we have as the first balancing condition (fig. 2)

$$P+L_3=(1+\alpha)(R+L_2), \quad . \quad . \quad . \quad . \quad (4)$$

and for the second (fig. 3)

$$P+L_2=(R'+L_3)/(1+\alpha) \quad . \quad . \quad . \quad . \quad (5)$$

Combining (4) and (5) we have

$$P=\frac{R+R'}{2}-\frac{\alpha}{2}\left\{\alpha(R+L_2)+(L_2-L_3)\right\} . \quad . \quad (6)$$

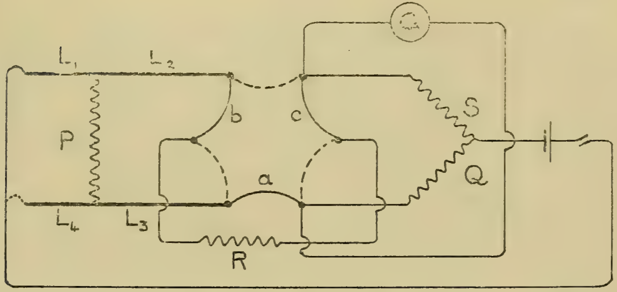
If Q is equal to S within 2 parts in 10,000, then $\alpha=0{\cdot}0002$ and P is equal to $(R+R')/2$ within 2 parts in 100 millions. This is on the assumption that $L_2=L_3$. If L_2 and L_3 each have a resistance of about 0·1 ohm but differ in resistance by 10 per cent., then the error introduced by neglecting α and taking the equation

$$P=(R+R')/2$$

as an exact one is equivalent to about 0°·0001 C. The want of equality of the leads and the want of equality of the ratio-coils may therefore be easily eliminated as sources of error.

Practical Application.—The reversals which have been indicated are conveniently made by means of a six-pole switch with connexions as shown in fig. 4. It is of course easy to arrange for the change in position of the battery lead to be made simultaneously.

Fig. 4.

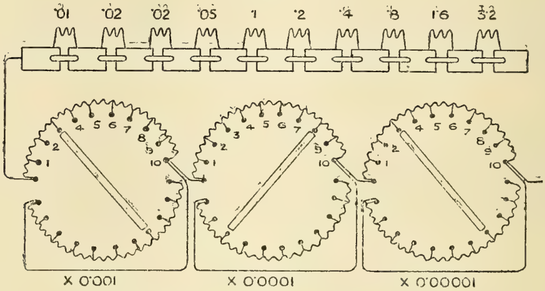


If the link *a* always forms a part of L_3, then *b* will always be in series with L_2 and *c* with R; equality of the resistances of the links *a, b, c* is then of no importance. Mercury contacts are employed.

As the method is practically useless unless R is a resistance capable of being changed in steps varying from 0·00001 ohm to several ohms, it is necessary to describe the construction of such a resistance in some detail. Messrs. Dickinson and Mueller * have already described a system capable of such changes, and a resistance-box based on that system was exhibited to the author by Messrs. Waidner and Burgess of the Thermometric Department of the Bureau of Standards, Washington. The author here expresses his thanks to Messrs. Waidner and Burgess for the great kindness shown to him on that and other occasions.

The system of resistances which we describe here has not, we believe, been previously used. Fig. 5 shows the arrangement. All the coils are of manganin, and those of 0·01 ohm and upwards (apart from the dials) have mercury contact-pieces, after the manner of those introduced by the Cambridge Scientific Instrument Co. The three dials are used to produce the small changes of resistance. In the case of the 0·001 ohm dial we have 10 resistances of 0·1 ohm each in series, and 10 resistances of 9·9 ohms each, also in series. The contact-brushes enable one or more of the 0·1 ohm resistances, each to be shunted by 9·9 ohms, and the shunting of each coil produces a diminution of the total resistance of 0·001 ohm. This device does not involve any very accurate adjustment of the coils, as will readily be seen. If the resistances are exactly 0·1 ohm and 9·9 ohms respectively, then when placed in parallel they will produce changes in the resistance for each step of the dial of exactly 0·001 ohm.

Fig. 5.



Variable Resistance. Method 1.

The resistance coils in the three dials are as follows:—for the 0·001 ohm dial, ten resistances of 0·1 ohm each and ten of 9·9 ohms each; for the 0·0001 ohm dial, ten resistances of 0·05 ohm and ten of 24·95 ohms; and for the 0·00001 ohm dial, ten resistances of 0·01 ohm and ten of 9·99 ohms.

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* Dickinson & Mueller, Bull. Bur. of Stands. vol. iii. no. 4, p. 646 (1907).

If, however, the coils are badly adjusted so that instead of a resistance being 9·9 ohms it is 9·95 ohms, the change when this coil was used as a shunt resistance would be 5 millionths of an ohm less than 0·001, but an error of this amount would not necessarily be made, as the bridge is very easily calibrated. Badly adjusted shunt coils are equivalent to a non-uniform slide wire. It will be seen that only ordinary care is required in the adjustment of the coils. In the application of the first method, there is, in addition to the three dials and in series with them, a coil of about 0·4 ohm resistance ; this, together with the resistance in the three dials (when reading 0 . 0 . 0), makes a total resistance of about 2 ohms.

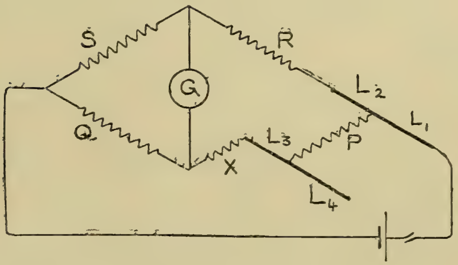
With such a resistance system for R the bridge may be standardized by inserting a standard coil of 2 ohms resistance in the place of P and obtaining a balance by shunting this coil, or by the use of the three dials. P and R are then reversed and a second balance obtained. This measurement enables the resistance of the arm R to be calculated when the dials read 0 . 0 . 0 and the other coils are shunted through the mercury contacts. To standardize the main resistance-coils a 10-ohm coil may be placed in P and R adjusted for a balance.

A complete calibration of R is most readily made in a manner similar to that used for the Callendar-Griffiths bridge, but the latter process need not be described here as it is so well known.

The resistances Q and S are conveniently of 200 ohms resistance.

Second Method.

Fig. 6.

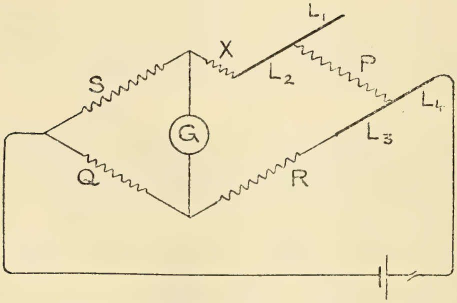


Principle.—At first the connexions are as shown in fig. 6, in which X is the adjustable resistance and is of a form similar to that described for R in Method I. Q, S, and R are maintained constant and balance is always obtained by an adjustment of X. The balancing condition is

$$P+L_3+X=Q(R+L_2)/S \quad . \quad . \quad . \quad . \quad (7)$$

X and R are now interchanged in position and the current is led into L_4 instead of L_1 (fig. 7).

Fig. 7.



When a balance is obtained we have

$$P+L_2+X'=S(R+L_3)/Q \quad . \quad . \quad . \quad . \quad (8)$$

X′ being the new value of X. If Q/S is nearly unity we have from equations (7) and (8)

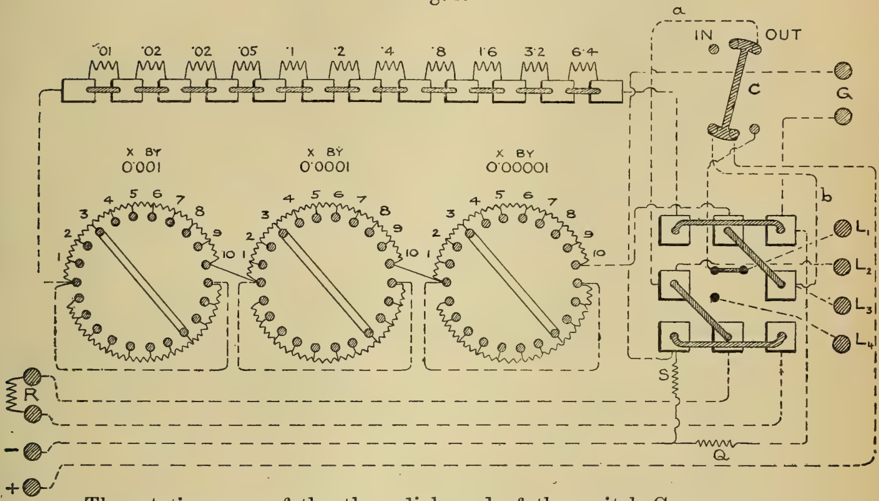
$$P=R-\frac{X+X'}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Any change in P is therefore balanced by a corresponding change in the opposite direction in X. If Q differs from S by 2 parts in 10,000 and L_2 and L_3 are about 0·1 ohm in resistance, then the leads of the thermometer will have to vary by 100 per cent. before an error so great as 0°·001 C. is introduced.

Practical Application.—A very useful form of bridge is that shown in fig. 8, in which all the coils are of manganin and the commutator has mercury contacts. It is convenient to make Q and S of about 190 ohms resistance, and they should be approximately equal. R is a coil of about 10 ohms for temperature measurements from 0° to 700° C.

The switch C is not an essential part of the apparatus, but it is convenient since it enables the value of R to be obtained in terms of X without disconnecting the platinum thermometer. The reading obtained is the "bridge centre" and can be taken at any time. Let the thermometer leads be connected to the bridge and suppose the switch C to be in the "out" position. Then for the two positions of the

Fig. 8.



The rotating arms of the three dials and of the switch C carry conducting straps which connect diametrally opposite studs. The switch C connects four studs together at one time. With C in the IN position and the commutator as shown in the figure, the connexions are those of fig. 6. With the commutator rotated 90° anti-clockwise the connexions are those of fig. 7. With the commutator and C (in OUT position) as shown in the figure the connexions are those of fig. 9; rotating the commutator 90° anti-clockwise now gives the connexions of fig. 10.

commutator the bridge connexions are as shown in figs. 9 and 10 (p. 560), the first balancing condition being

$$X+b'=\frac{Q}{S}(R+a'), \quad . \quad . \quad . \quad . \quad (10)$$

and the second

$$R+b'=\frac{Q}{S}(X'+a'), \quad . \quad . \quad . \quad . \quad (11)$$

where a' and b' have values slightly smaller than a and b respectively due to the shunting of the portion $(a+b)$ by the portion (L_2+P+L_3). Since $\frac{Q}{S}$ is nearly unity we have with great accuracy

$$2R = X + X' = \text{a constant}^* \quad . \quad . \quad . \quad . \quad (12)$$

Fig. 9.

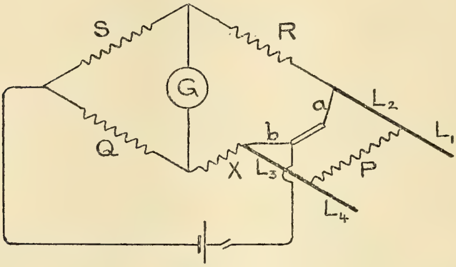
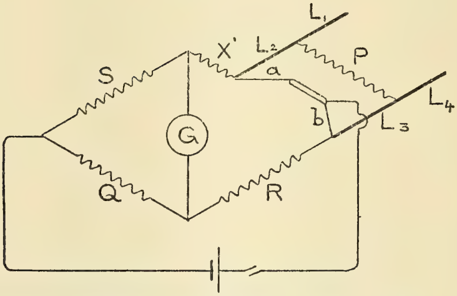


Fig. 10.



Now, when the switch is placed in the "in" position we have (see equation (9))

$$2P = 2R - (X'' + X'''), \quad . \quad . \quad . \quad . \quad (13)$$

that is, the difference between the mean values of X in the two measurements is the resistance of P, and all subsequent changes in the resistance of the thermometer bulb are equal to the corresponding changes in the mean value of X.

With this bridge if one accumulator is used for the production of the current, the current through the platinum thermometer will be about 0·01 ampere, and *remains constant at all temperatures* owing to the constancy (apart from the small variations in the resistance of the leads) of the arms of the bridge. This has already been shown to be of advantage in precision measurements.

We have used both Methods 1 and 2 for the measurement of resistance and have found, as will be anticipated, that the measurements are simpler when the leads from P are nearly equal in resistance. When a series of measurements have to be made—as in thermometric work—it will be a great help to have a small variable resistance in circuit with one of the leads so as to adjust L_2 and L_3 to near equality.

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* The resistance R is best chosen so that practically the whole of the resistance X is in series when the switch is in the "out" position.

Having once designed a suitable adjustable resistance, such as that described for R (Method 1) and X (Method 2), it is possible to develop very many bridge methods suitable for the measurement of a resistance with current and potential leads. In addition to the two low resistance bridges which we have described we have developed two other low resistance bridges, but they are not described as they are not so convenient in practice. In addition the method described by Dr. Searle [*] might be used for precise work, but in such a case the ratio coils should be exactly equal and the galvanometer connexions should be reversed for the second balance in order to keep the current through the galvanometer, due to any thermal E.M.F. in P, constant in direction. Even then there is some disturbance owing to the changes in the resistances of the bridge arms, but the method is of considerable value.

The chief points in connexion with the two bridges we have described are:—

(1) No slide wire and therefore no thermal E.M.F. at contact, and no variable contact resistance in galvanometer branch.

(2) The variable resistance may be rapidly adjusted to obtain a balance.

(3) As the galvanometer circuit is always closed, no thermal key is required.

(4) The resistance of the thermometer leads is eliminated as a source of error.

(5) Secular changes in the resistance of the thermometer "bulb" or "spiral" may be detected with certainty.

(6) With Method 2 the current through the thermometer is the same at all temperatures without adjustment of any external resistance.

Third Method.

Of the methods so far described we believe that Method 2 is the most convenient, although very slightly less sensitive than Method 1. One feature of the bridges to which objection may be taken is the use of mercury contacts for many of the coils. This objection may be disregarded when measurements of the highest precision are being made, but it has been pointed out to us that for many measurements a dial resistance bridge would be exceedingly convenient. Two such resistance bridges are therefore described here.

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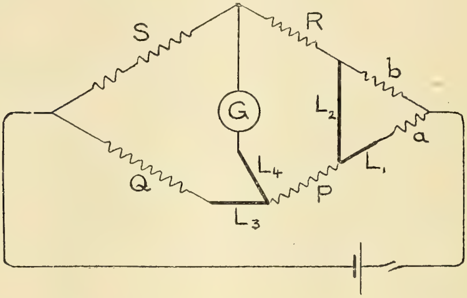
[*] Searle, 'The Electrician,' March 31 to April 21, 1911, Section 26.

In the Third Method, one of the leads of the platinum thermometer is shunted so as to form a resistance system similar to that of the Kelvin double bridge. The ratio of the two shunt resistances $(a+L_1)$, and b (fig. 11) is not, however, the same as the ratio of $(Q+L_3)$ to S, but differs from it by an amount depending on the ratio of R to S. In the figure (11) P is the platinum thermometer and L_1, L_2, L_3, and L_4 the leads. When the bridge is balanced the value of P is given by

Fig. 11.



$$P=\frac{QR}{S}+\frac{RL_3}{S}+\frac{bL_2}{(a+b+L_1+L_2)}\left(\frac{Q+L_3}{S}-\frac{a+L_1}{b}\right). \quad (10)$$

In practice b is made equal to S, and a and Q are made large compared with L_1, L_2, L_3, and L_4. If we at first suppose that $L_1=L_2=L_3=L_4$, then we have as a very close approximation

$$P=\frac{QR}{S}+L_1\left\{\frac{R}{S}+\frac{b}{S}\frac{Q}{(a+b)}-\frac{a}{(a+b)}\right\}$$

$$=\frac{QR}{S}+L_1\left\{\frac{a(R-S)+b(R+Q)}{S(a+b)}\right\}. \quad . \quad (11)$$

Hence if a is equal to $b\frac{(R+Q)}{(S-R)}$ we have the simple relation

$$P=\frac{QR}{S}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Q is the variable arm of the bridge, and hence a must automatically change with Q if the relation $a=b(R+Q)/(S-R)$ is always to be satisfied. Fortunately, this is easily possible, as will presently be seen.

It is now necessary to indicate the most favourable values for the constant arms of the bridge, and to get an idea of the probable errors introduced by assuming $P=QR/S$ to be an exact equation.

We suggest as values for the arms of the bridge

$$R=1 \text{ ohm.}$$
$$S=100 \text{ ohms.}$$
$$b=100 \text{ ohms.}$$

Q and a are variable arms, the value of Q being about 254 ohms when P, the platinum thermometer, has a resistance of 2·54 ohms.

With regard to the probable errors we will consider two cases: (1) when the thermometer leads are equal in resistance, (2) when they are not equal.

For this purpose equation (10) is conveniently recast in the form

$$P=\frac{QR}{S}+\frac{RL_3}{S}+\frac{L_2}{(a+b+L_1+L_2)}\left(\frac{b}{S}Q-a+\frac{b}{S}L_3-L_1\right), \quad . \quad (13)$$

Substituting a value for Q obtained from the relation $a=b(R+Q)/(S-R)$, we obtain

$$P=\frac{QR}{S}+\frac{R}{S}\left\{L_3-L_2\frac{(a+b)}{(a+b+L_1+L_2)}\right\}-L_2\left(1-\frac{a+b+L_2+\frac{b}{S}L_3}{a+b+L_1+L_2}\right). \quad . \quad (14)$$

The nominal value of R/S is 0·01, that of b/S is 1·0, of L_1, L_2, L_3, and L_4, 0·15 ohm, and the minimum value of $(a+b)$ is 354 ohms. Hence, if $L_1=L_2=L_3$, the total value of all the terms after $\frac{QR}{S}$ cannot exceed $0{\cdot}000001_4$ ohm, corresponding to a little more than one ten-thousandth of a degree. If now L_1, L_2, and L_3 differ in resistance by 1 per cent., a total error of $0{\cdot}00001_5$ ohm or $0^\circ{\cdot}001_5$ C. is introduced. As the leads are readily adjusted within much less than 1 per cent., we may take the simple equation

$$P=QR/S$$

to be sufficiently correct.

We have now to consider the best means of arranging the bridge coils so that a shall equal $b(\mathrm{R}+\mathrm{Q})/(\mathrm{S}-\mathrm{R})$ whatever the value of Q. Since $b=100$, $\mathrm{S}=100$, and $\mathrm{R}=1$, we may write

$$a=\frac{100(\mathrm{Q}+1)}{99}=\frac{\mathrm{Q}+1}{0{\cdot}99}.$$

If, therefore, the a coils be made equal to $\frac{1}{0{\cdot}99}$ times the Q coils, and in addition a $1/0{\cdot}99$ ohm coil be placed so as to be always in series with them, it follows that if the a and Q coils are arranged in dials so that one cannot be varied without the other, the relation $a=b(\mathrm{R}+\mathrm{Q})/(\mathrm{S}-\mathrm{R})$ must always hold.

Fig. 12.

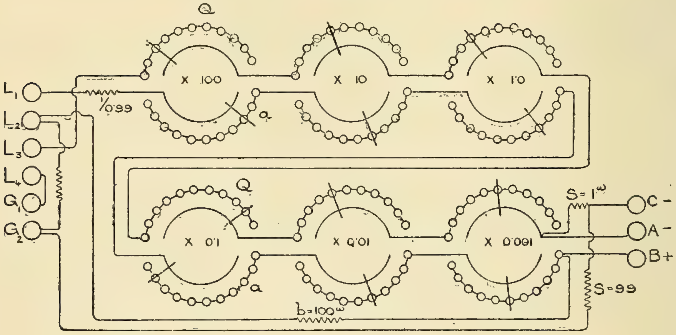


Fig. 12 shows the general arrangement of the bridge. The resistances Q and a are arranged in six dials with good brush contacts, an a coil being equal to $\frac{1}{0{\cdot}99}$ times the corresponding Q coil. S consists of two coils in series, one of 99 ohms and one of 1 ohm. The object of thus splitting S into two parts is to be able to rapidly check the bridge to see if the equation

$$a=b(\mathrm{R}+\mathrm{Q})/(\mathrm{S}-\mathrm{R})$$

is sufficiently true for all possible values of Q. To make the check, the position of the current lead is changed from A to C and short-circuiting straps of copper connect terminal L_2 to G_2 and L_1 to L_3 and G_1. Fig. 14 now shows the scheme of connexions. Fig. 13 shows the usual scheme with P connected to the bridge.

Fig. 13.

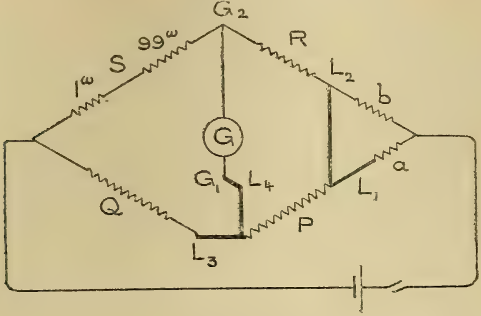
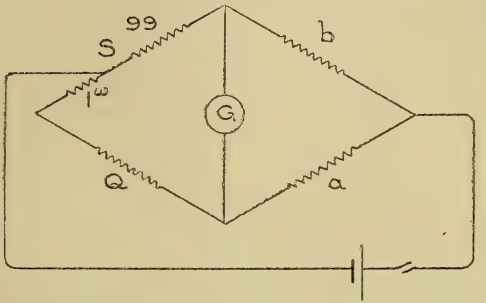


Fig. 14.



With the connexions as in fig. 14 the condition for balance is that a shall equal $b(\mathrm{Q}+1)/(\mathrm{S}-1)$. Q (and of course a) may now be rapidly varied from 200 ohms upwards by operating the dials, and if the bridge remains balanced we know that the condition of equality is satisfied for all possible measurements with the bridge. In practice this balance should remain good within 1 part in 10,000 for measurements within 0°·001 C. Clearly the coils of the first two dials should be carefully adjusted.

To *standardize* the bridge, standard resistance-coils with current and potential leads are substituted for the platinum thermometer, the connexions being identical with those when a measurement of temperature is being made. It is of interest to note that it is the ratio QR/S which is standardized and not Q.

To *calibrate* the bridge an adjustable resistance is substituted for the thermometer and a method similar to that employed for the Callendar-Griffiths bridge is used.

The Dial Contacts.—For precision work it is necessary for the dial contact resistances to be fairly reproducible, and this involves well-designed brushes and good workmanship. Before attempting to design a dial-form bridge we made some experiments on the constancy of the contact resistances in a Wolff potentiometer, and satisfied ourselves that the contact resistances in six well-made dials in series will keep constant within about 0·0002 ohm over a period of twelve months. Mr. Whipple, of the Cambridge Scientific Instrument Co., has very kindly given us values approximating to the contact resistance of a special form of brush made by them. The resistance was measured from below the stud of a dial, through the brush contact to a position on the brush ring. The *contact resistance* is therefore less than any of the values cited. With vaseline on the contacts the resistances were found to remain very constant, and on similar studs the values measured were :—

No. 1.........	0·000289 ohm.
„ 1.........	0·000280 „
„ 2.........	0·000288 „
„ 2.........	0·000289 „

In each case the second reading was taken after rubbing over the stud ten times. These results are most gratifying. In the 6-dial bridge (fig. 12) it would be necessary for a *variation* of 0·001 ohm (*i. e.* nearly four times a single contact resistance) to result to produce an error equivalent to 0°·001 C.

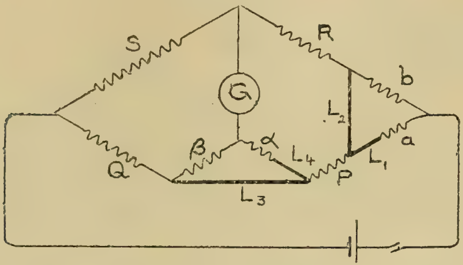
The fact that the adjustable resistances are arranged in a dial form renders the bridge particularly useful where rapid observations are necessary. The galvanometer circuit is permanently closed, so that thermal E.M.F's produce a minimum of disturbance, and the sensitiveness of the bridge is practically as great as any combination of resistances hitherto used for the measurement of temperature by means of a platinum thermometer. For general use a galvanometer of from 5 to 20 ohms resistance may be used.

Fourth Method.

In this the leads of the platinum thermometer are practically eliminated by shunting two of them with suitable resistances after the manner of the Kelvin double bridge. The connexions are shown in fig. 15.

The thermometer has four leads L_1, L_2, L_3, and L_4. L_2 is shunted by $b+a+L_1$ and L_3 is shunted by $\beta+\alpha+L_4$.

Fig. 15.



When the connexions are as shown in the figure the condition for balance is

$$\frac{P+\dfrac{(\alpha+L_4)L_3}{\alpha+\beta+L_3+L_4}+\dfrac{(a+L_1)L_2}{a+b+L_1+L}}{Q+\dfrac{\beta L_3}{\alpha+\beta+L_3+L_4}}=\frac{R+\dfrac{bL_2}{a+b+L_1+L_2}}{S} \quad . \quad . \quad (15)$$

and the expression for P is

$$P=\frac{QR}{S}+\frac{\beta L_3}{\alpha+\beta+L_3+L_4}\left(\frac{R+\dfrac{bL_2}{a+b+L_1+L_2}}{S}-\frac{\alpha+L_4}{\beta}\right)$$

$$+\frac{bL_2}{a+b+L_1+L_2}\left(\frac{Q}{S}-\frac{a+L_1}{b}\right) \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In practice the second and third terms on the right hand side of equation (16) are made negligibly small and then

$$P=QR/S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In setting up the bridge the resistances are so chosen that approximately $R/S=\alpha/\beta$ and $\frac{Q}{S}=\frac{a}{b}$. In the general case the bridge is *set* before commencing measurements of temperature. To do this α is disconnected from L_4, and by adjustment of Q and a a balance is obtained whether L_2 is connected to Rb or not. The following two equations then hold good :—

$$\frac{P+L_3+a+L_1}{Q}=\frac{R+b}{S}, \quad . \quad . \quad . \quad (18)$$

and

$$\frac{P+L_3+(a+L_1)\left(\dfrac{L_2}{a+b+L_1+L_2}\right)}{Q}=\frac{R+b\left(\dfrac{L_2}{a+b+L_1+L_2}\right)}{S} \quad . \quad . \quad . \quad . \quad (19)$$

From (18) and (19) we have

$$\frac{a+L_1}{b}=\frac{Q}{S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Afterwards, by further adjustments of Q and a and of α or β, a balance is obtained which holds good whether L_3 is connected to $Q.\beta$ or not. In these circumstances

$$\frac{P+\alpha+L_4+\dfrac{(a+L_1)L_2}{a+b+L_1+L_2}}{Q+\beta}=\frac{R+\dfrac{bL_2}{a+b+L_1+L_2}}{S}, \quad . \quad . \quad (21)$$

and the relation (15) also holds. From (15) and (21) we have

$$\frac{\alpha+L_4}{\beta}=\frac{R+\dfrac{bL_2}{a+b+L_1+L_2}}{S}, \quad . \quad . \quad . \quad (22)$$

and from (15), (20), and (22) it follows that

$$P=QR/S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

This preliminary setting of the bridge is, in practice, comparatively easy, but if the arms of the bridge are carefully chosen it is not necessary, even in precision work.

For the purposes of thermometric measurements with a thermometer of 1 ohm fundamental interval, it is convenient to choose as nominal values :—$R=5$ ohms, $S=500$ ohms, $\alpha=9{\cdot}85$ ohms, $\beta=1000$ ohms, and $b=500$ ohms. Q and a are equal variable resistances and are automatically changed together.

If the preliminary setting of the bridge is dispensed with, the probable errors that are likely to be introduced, because of it, are best seen from a consideration of the following equation, which is another form of (16)

$$\begin{aligned}P=\frac{QR}{S}&+\frac{\beta L_3}{\alpha+\beta+L_3+L_4}\left(\frac{R}{S}-\frac{\alpha+L_4}{\beta}\right)\\&+\frac{bL_2}{a+b+L_1+L_2}\left[\left(\frac{Q}{S}-\frac{a}{b}\right)+\left(\frac{\beta L_3}{S(\alpha+\beta+L_3+L_4)}-\frac{L_1}{b}\right)\right]\\&\qquad . \quad . \quad . \quad . \quad (24)\end{aligned}$$

Let us suppose that measurements are to be made at 0° C. Then the value of P is about 2·5 ohms and Q and a will each be about 250 ohms. If the resistance of each lead of the platinum thermometer is of the order of 0·15 ohm the value at 0° C. of $\beta L_3/(\alpha+\beta+L_3+L_4)$ is about 0·15, and the value of $bL_2/(a+b+L_1+L_2)$ is about 0·10. With increasing temperature the value of the first ratio will slightly increase and that of the second ratio will diminish. As $R/S=0{\cdot}01$ very nearly it follows that if $\frac{R}{S}$ is equal to $(\alpha+L_4)/\beta$ *within 1 per cent.*, the value of the second term on the right hand side of equation (24) cannot exceed $0{\cdot}00001_5$ ohm, which corresponds to $0^{\circ}{\cdot}001_5$ C. Hence, if the resistance-coils have the values already stated, the lead L_4 may vary in resistance from 0·09 to 0·21 ohm before a correction equal to 0°·001 C. has to be applied.

At 0° C. the ratio Q/S is about 0·5, and it is necessary for Q/S to be equal to a/b within 1 part in 5000 in order that the correction $\frac{bL_2}{(a+b+L_1+L_2)}\left(\frac{Q}{S}-\frac{a}{b}\right)$ may not be greater than 0°·001 C. As Q, S, a, and b are resistance-coils and include no leads, such equality in the ratios may readily be obtained.

With regard to the last term of equation (24), as the ratio $bL_2/(a+b+L_1+L_2)$ is about 0·10 and the ratios $\beta L_3/S(\alpha+\beta+L_3+L_4)$ and L_1/b are each about 0·0003, it is necessary for L_1 to differ from L_3 by 30 per cent. before an error so great as 0°·001 C. could be introduced because of the inequality. In practice we may safely assume that the equality will be within less than 1 per cent. and so may dismiss the correction from consideration.

As a convenient summary it may be stated :—If the resistance of each of the leads of the platinum thermometer be not greater than 0·15 ohm, and if the ratio R/S is equal to $(\alpha+L_4)/\beta$ within 4 parts in 1000 and the ratio Q/S is equal to a/b within 1 part in 10,000, no greater total error than that corresponding to 0°·001 C. will result by neglecting all the terms after the first on the right side of equation (16). The bridge is then used as if it were a simple Wheatstone bridge having the arms P, Q, R, and S. No preliminary setting need be made. The resistances of the leads of the platinum thermometer should be approximately equal, but a difference of 30 per cent. produces an error of 0°·001 C. only. If the preliminary balancing of the bridge is made there is no error due to any inequalities of leads or ratios.

The construction of the bridge should be much on the same lines as that described for the Third Method, there being six dials for the Q and a coils.

LII. *The Theory of Photoelectric Action.* By O. W. Richardson, *Professor of Physics, Princeton University* *.

IN a recent paper † the writer has developed a theory of photoelectric phenomena which is based on thermodynamic and statistical principles. It has been shown that the number N of electrons emitted from unit area of a body in equilibrium with the complete radiation characteristic of its temperature θ may be expressed in either of the two equivalent forms :

$$N = \frac{c}{4}\int_0^\infty \epsilon F(\nu, \theta)\, E(\nu, \theta) d\nu \quad . \quad . \quad . \quad . \quad (1)$$

and

$$N = \alpha A \theta^{1/2} e^{\int \frac{w}{R\theta^2} d\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $E(\nu, \theta)$ is the function which expresses the distribution in the spectrum of the steady energy density, $\epsilon F(\nu, \theta)$ is the number of electrons emitted in the presence of unit energy whose frequency lies between ν and $\nu + d\nu$, c is the velocity of light, A is a constant characteristic of the substance and independent of θ, α is the proportion of the returning electrons which are absorbed (*i. e.* not reflected), w is the internal latent heat of evaporation of one electron, and R is the gas constant for one molecule.

The right-hand sides of (1) and (2) must be identical functions of θ since they are true for all values of this variable. If we may assume $E(\nu, \theta)$, α and w to be known functions of ν and θ in so far as they involve these variables, the problem of finding the function $\epsilon F(\nu, \theta)$ resolves itself into that of solving an integral equation. There is also a similar equation involving the energy T_ν of the emitted particles instead of the number of them. The solutions which make $\epsilon F(\nu)$ and T_ν capable of representation by a single analytic function of ν throughout the range from zero to infinity have already been considered. It appears that these solutions do not exist when $E(\nu, \theta)$ has the form given to it by Planck or the approximation for Planck's formula which is used below. The object of the present communication is to indicate another type of particular solution. Reasons will be given in a later paper for believing that this second type of solution is the one which actually represents the facts.

Such experiments as have been made on this subject indicate that $\epsilon F(\nu, \theta)$ is practically independent of θ, so that we should expect $\epsilon F(\nu, \theta)$ to be a function of ν only. We shall assume that we can put

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* Communicated by the Author.

† Phys. Rev. vol. xxxiv. p. 146 (1912); Phil. Mag. vol. xxiii. p. 615 (1912).

$$w = w_0 + \tfrac{3}{2} R\theta$$

where w_0 is independent of θ. As yet, this equation has only been justified as a convenient approximation. For the present we shall also assume that $\alpha = 1$, *i. e.* that there is no reflexion of the incident electrons. This assumption has probably more serious physical consequences than any of the others when the results come to be applied to the behaviour of real matter. Under these circumstances equation (2) reduces to

$$N = A\theta^2 e^{-\frac{w_0}{R\theta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the radiation formula we shall assume

$$E(\nu, \theta) = \frac{8\pi}{c^3} h\nu^3 e^{-\frac{h\nu}{R\theta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It can be shown that the replacement of Planck's formula by (4) only introduces inaccuracies in the final results which are proportional to $e^{-\frac{w_0}{R\theta}}$. This is a very small proper fraction. The integral equation to be solved is now reduced to

$$\int_0^\infty \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{R\theta}} d\nu = A_1 \theta^2 e^{-\frac{w_0}{R\theta}}, \quad . \quad . \quad . \quad (5)$$

where

$$A_1 = \frac{c^2}{2\pi} A.$$

This is satisfied by

$$\left.\begin{aligned} &\epsilon F(\nu) = 0 && \text{when} \quad 0 < h\nu < w_0 \\ \text{and} \quad &\epsilon F(\nu) = \frac{A_1 h}{R^2 \nu^2}\left(1 - \frac{w_0}{h\nu}\right) && \text{when} \quad w_0 < h\nu < \infty \end{aligned}\right\} \quad . \quad . \quad (5a)$$

This is of the general form, $\frac{A_1}{\nu^2} \times$ a universal function of $\frac{w_0}{h\nu}$, which was previously specified ; it is not, however, the same analytic function of ν throughout the range from 0 to ∞.

It shows very clearly that there is a limiting value

$$\nu_0 = \frac{w_0}{h},$$

below which there is no photoelectric emission at all. This is in accordance with the results of experiments.

The index 2 of θ on the right of (3) and (5) depends on the various approximations which have been made. In general it will depend on the specific heat of electricity σ and the way in which α and σ depend upon the temperature. Now it may be shown that unless the index of θ is an integer there is no solution of the type

$$\epsilon F(\nu) = 0 \quad \text{when} \quad 0 < h\nu < w_0$$

and

$$\epsilon F(\nu) = \frac{A_1}{\nu^2} \phi \left(\frac{w_0}{h\nu}\right) \quad \text{when} \quad w_0 < h\nu < \infty.$$

It follows that if this type of solution is upheld by experiment, there must be some undiscovered relation between the temperature variation of photoelectric effects, the specific heat of electricity, and the reflexion of electrons as a function of the temperature, which makes the index an exact integer. We have not enough information, particularly in regard to the photoelectric effect, to make it profitable to speculate further about this relation at present. The point, however, is important since it shows that the solutions have a generality which is not limited by the somewhat peculiar physical approximations which have been made.

It is possible that the index of θ on the right of equation (5) might be some positive integer λ other than 2. The solutions may be readily obtained by substituting a series of powers of ν for $\epsilon F(\nu)$, integrating from $\frac{w_0}{h}$ to ∞, and comparing coefficients of θ. As the general case does not appear to possess special features, it is simpler, and otherwise as satisfactory, to keep to the particular case $\lambda = 2$, which is much the most likely value of the index.

We shall now consider the average kinetic energy T_ν of the electrons which are emitted by light of frequency ν. The total energy E emitted under the influence of the complete radiation at θ is clearly

$$E = \frac{c}{4} \int_0^\infty T_\nu \epsilon F(\nu) \, . \, E(\nu, \theta) d\theta. \quad . \quad . \quad . \quad (6)$$

An elementary calculation shows that the energy streaming towards the metal in unit time by virtue of the thermal motion of the external electrons is $2NR\theta$. Of this energy let the proportion $1-\beta$ be reflected, then β is the proportion which is absorbed. For equilibrium we have therefore

$$E = \beta \, . \, 2NR\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we neglect the effects of reflexion, by putting

$$\alpha = \beta = 1,$$

and substitute the value of N from (2), making the same approximations as before, we obtain from (6) and (7)

$$\int_0^\infty d\nu \, . \, T_\nu \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{R\theta}} = 2A_1 R\theta^3 e^{-\frac{w_0}{R\theta}}.$$

Subject to

$$\epsilon F(\nu) = 0 \text{ from } \nu = 0 \text{ to } \nu = \frac{w_0}{h}$$

and

$$\epsilon F(\nu) = \frac{A_1 h}{R^2 \nu^2}\left(1 - \frac{w_0}{h\nu}\right) \text{ from } \nu = \frac{w_0}{h} \text{ to } \nu = \infty,$$

the solution of this is

$$T_\nu = h\nu - w_0 \text{ when } w_0 < h\nu < \infty. \quad . \quad . \quad . \quad (8)$$

For values of $h\nu$ which lie between 0 and w_0, T_ν has no meaning, as the corresponding electrons have no external existence.

The solution (8) is dependent on the assumption that the reflexion of electrons can be neglected. This is equivalent to assuming that effects which arise from the collisions of the electrons may be disregarded. But if we consider this from the point of view of the electrons emitted under the influence of the light, we see that neglecting the effects of collisions is tantamount to assuming that the only energy lost by the electrons is used up in overcoming the work w_0 of the forces which tend to retain them within the interior of the substance. Under these circumstances the kinetic energy of the escaped electrons will be equal to that which they acquire by the action of the light (not necessarily from the light directly) minus the work w_0 which they have to do to escape. It is clear that the energy which they acquire under the influence of light is $h\nu$ where h is Planck's constant. It evidently has the same value for all the electrons liberated by light of the same frequency; any difference in the energy of the electrons liberated by monochromatic light must therefore be attributed to the effect of collisions of the escaping electrons in the interior of the substance.

We can take account of the reflexion of electrons tentatively by putting $\beta = s\alpha$. Then, instead of (8), we get

$$T_\nu = s(h\nu - w_0) \text{ when } w_0 < h\nu < \infty. \quad . \quad . \quad . \quad (9)$$

For small velocities of incident electrons, such as those with which we are dealing, the proportion reflected increases with increasing energy. It follows that out of a mixed aggregate of incident electrons a greater proportion of the slow ones will be absorbed than of the fast ones, and that the proportion of incident electrons which is absorbed will be greater than the proportion of their incident energy which is absorbed. Thus s will be a positive quantity which is less than unity.

Equations (8) and (9) are independent of the particular value of the index 2 of θ in equation (3). These equations and the first part of (5 a), have been verified by experiments made by Dr. K. T. Compton and the writer *. A fuller account of these experiments will shortly be published in this journal †.

Palmer Physical Laboratory,
Princeton, N.J.

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* Science, vol. xxxv. p. 783, May 17, 1912.

† *Note added during correction of proof.*

There do not at present appear to be any considerations which would necessarily limit the applicability of the above methods, and the results to which they lead, to the comparatively narrow field to which the term photoelectric effect is usually restricted. For instance, there is no conclusive reason why they should not be applicable to the ionization produced by such radiations as the Röntgen and γ rays, if these differ from light only in degree and not in kind. Moreover, the deduction makes no essential use of the fact that the particles have been supposed to be electrically charged; so that somewhat similar laws may be expected to characterize the reversible formation of gaseous chemical products under the influence of aethereal radiations.

Equations (1) to (9) have been derived without making use of the hypothesis that free radiant energy exists in the form of " Licht-quanten," unless this hypothesis implicitly underlies the assumptions :—(A) that Planck's radiation formula is true ; (B) that, *ceteris paribus*, the number of electrons emitted is proportional to the intensity of monochromatic radiation. Planck (*Ber. der Deutsch Physik. Ges.* 1912) has recently shown that the unitary view of the structure of light is not necessary to account for (A) and it has not yet been shown to be necessary to account for (B). It appears therefore that the confirmation of equations (5 a), (8) and (9) by experiment would not necessarily involve the acceptance of the unitary theory of light.

The essence of the foregoing discussion has already been printed in ' Science ' (vol. xxxvi. p. 57, 1912).

In a recent paper Einstein (*Ann. der Physik*, vol. xxxvii. p. 832, 1912) has come to the conclusion that when a gas decomposes under the influence of light of frequency ν there is an absorption of energy $h\nu$ for each molecule or electron emitted. Einstein's argument appears also not to be dependent on the unitary hypothesis, at any rate explicitly.

LIII. *The Photoelectric Effect.* *By* O. W. RICHARDSON and KARL T. COMPTON, *Princeton University* *.

[Plate XIII.]

PROBABLY there is no line of investigation more likely to lead to a correct understanding of the phenomena of photoelectric action than a careful determination of the relations between the nature of the metal, the frequency of the light, and the kinetic energy of the liberated electrons. A large amount of work has been done in the attempt to determine these relations, but the results have been very contradictory. For instance, von Baeyer and Gehrts †, and Klages ‡ found, in the case of several metals, that the maximum initial velocity of the electrons was independent of the metal used. Ladenburg § and other physicists have decided that the electronegative metals give off electrons with the greatest velocities; whilst Millikan and Winchester ‖ concluded that the initial velocity bears no relation to the Volta series. Most physicists who have investigated the subject believe that the maximum initial kinetic energy is a linear function of the frequency of the light; but some ¶ have obtained results supporting the view that the maximum velocity varies as the first power of the frequency.

The results of the present investigation show that there is a much greater unity in the relations between different metals and wave-lengths than has hitherto been supposed. In fact, it will be shown that the important features of the photoelectric behaviour of any metal are determined by a single parameter characteristic of the metal. The parameter has the dimensions of a frequency, and its significance will be explained later.

The first part of the paper is a discussion of the experimental data. These data may be of value in testing any theory of photoelectric action. In the latter part of the paper the results are applied to test the theories of these effects which have been developed by Einstein ** and by one of the authors ††.

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* Communicated by the Authors.

† *Ber. der Deutsch Physik. Ges.* xxi. p. 870 (1910).

‡ *Ann. der Physik,* vol. xxxi. p. 343 (1909).

§ *Verh. der Deutsch Physik. Ges.* ix. p. 504, *ibid.* p. 165 (1907); *Phys. Zeits.* vol. viii. p. 592 (1907).

‖ Phil. Mag. vol. xiv. p. 185 (1907).

¶ Kunz, Phys. Rev. vol. xxxi. p. 536 (1910), vol. xxxiii. p. 208 (1911).

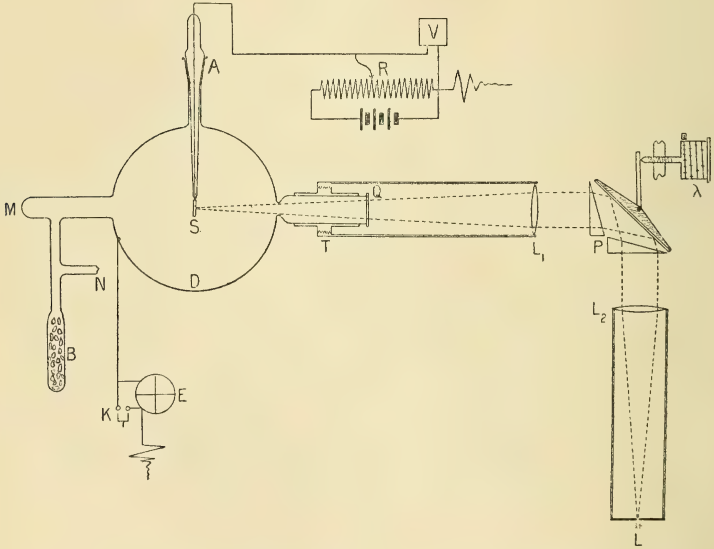
** *Ann. der Physik,* vol. xvii. p. 146 (1905).

†† Phys. Rev. vol. xxxiv. p. 146 (1912); Phil. Mag. vol. xxiii. p. 615 (1912); Science, vol. xxxvi. p. 57 (1912).

The main points wherein the present investigation differs from the earlier work on this subject are as follows:—(1) The contact difference of potential between the emitting and receiving electrodes is allowed for*. (2) The photoelectric cell is placed in position in an arm of a new type of monochromatic ultra-violet illuminator, made by Adam Hilger Ltd., of London, which is a distinct advance as a method of producing accurate and powerful illumination by monochromatic ultra-violet light. (3) The peculiar form of the photoelectric cell practically eliminates electron reflexion without the use of a screen and an auxiliary field, and at the same time it enables the distribution of total kinetic energy to be measured instead of simply the distribution of the velocity component normal to the emitting electrode.

The apparatus used is shown in fig. 1. The emitting electrode consists of a strip S of metal foil about 1 mm. wide and 5 mm. long placed at the centre of a glass bulb D of 7·5 cm. diameter. This bulb is silvered on its inner surface. It is connected with an electrometer having a sensibility of 936 divisions per volt, and acts as the receiving electrode. The strip S is held in position by a thin platinum wire sealed in a small glass tube, and is introduced through the ground-

Fig. 1.



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* See K. T. Compton, Phil. Mag. vol. xxiii. p. 579 (1912).

glass joint A. The neck of this bulb is closed by a quartz window Q. It is waxed firmly in a brass collar which screws into the telescope tube of the monochromatic illuminator at T, in such a position that the slit L is just focussed on the strip S so that the image of the slit for any particular wave-length of light may be made to coincide with the position of the strip. The final adjustment is made by using visible light as the source and looking through M. The strip S is shifted a little until it just shuts out the image. By turning the screw-head λ any desired wave-length may be thrown on S and its magnitude read off on the graduated scale. In the figure the illuminator is shown rotated through a right angle from its true position, about the axis of the telescope. The collimator should project out perpendicular to the plane of the paper. A quartz mercury lamp at L was used as the source of light. The apparatus was evacuated by a Gaede pump connected at N, and usually the tube B of coconut charcoal was used to obtain a still better vacuum.

The velocities of the liberated electrons were determined by varying the field between S and D by adjusting the sliding contact R, and the applied field was read directly from the voltmeter V. The distribution of velocity curves were obtained in the ordinary way.

The peculiarities of this apparatus are that the field between S and D is approximately radial, and that the area of the emitting electrode is very small compared with the area of the receiving electrode. In the first place, this arrangement makes it possible to measure the distributions of velocity of all the electrons irrespective of their angles of emission from S, and thus it gives the distribution of total energy of the electrons. In the second place. it makes the effect of electron reflexion practically negligible. A certain percentage of the electrons reaching D are reflected, this reflexion being diffuse. But none of these reflected electrons will return to S, except a very small proportion which start almost straight towards S. All the others will traverse comet-like paths past S and again strike D.

The metal strip to be tested was carefully scraped with a clean knife-blade. It was then placed quickly in position and the vacuum-pump started. The readings were taken as soon as the requisite vacuum was obtained.

The Distribution of Velocities.

The general character of the distribution of velocity curves is the same for all the metals, so that it will be sufficient to consider in detail the case of platinum only. With this metal readings were taken for wave-lengths 25, 23, and 21. The unit of wave-length is 10^{-6} cm. The readings are shown in Table I. V is the externally applied potential difference, R is the deflexion in scale-divisions per minute, and C is this deflexion reduced to a scale of 100 for the maximum deflexion. These readings may be taken as typical of all the distribution of velocity curves that we have obtained.

It is necessary to correct these readings for contact difference of potential. The method of determining this correction will be described later. After being thus corrected the numbers in Table I. are plotted thus:—○ in fig. 2 (Pl. XIII.). The significance of these curves may be explained as follows:—Take, for instance, the curve for 23 λ. The ordinate at −0·5 volt is 44. This means that 44 per cent. of the electrons are liberated with velocities equal to or greater than that velocity which gives them sufficient energy to overcome an opposing difference of potential of 0·5 volt.

Table I.

	λ = 25.		λ = 23.		λ = 21.	
V.	R.	C.	R.	C.	R.	C.
+ 2	41	98	78	100	31	100
1	42	100	78	100	31	100
0·5	41	98	78	100	31	100
0·2	42	100	78	100	31	100
0·1	42	100	78	100	31	100
0·05	42	100				
0·0	40	95	76	97	30·5	98·5
− 0·1	27	64	68	87	29	93
0·2	9	22	54	69	26	84
0·3	3	7	44	56·5		
0·4	0	0	30·5	39	21	68
0·5	...	...	19	24		
0·6	...	...	8	10	15	48
0·7	...	...	1·5	2		
0·8	...	...	0	0	8·5	27
0·9	...	...	...	...	6·5	19
1·0	...	...	...	...	3	10

To obtain the relative number which are emitted with any given energy, we must differentiate these curves with respect to V. The result of this differentiation is shown in fig. 3. For wave-length 25 the number emitted with an energy corresponding to 0·2 volt is to the number corresponding to 0·1 volt as the ordinate in fig. 3 at 0·2 volt is to the ordinate at 0·1 volt, or as 90 is to 65, and so on.

An examination of these curves leads to a number of interesting conclusions.

(1) The maximum energy, expressed in volts, is a linear function of the frequency of the exciting light, within the limits within which the results of the experiments are consistent.

(2) The curves appear to be almost symmetrical with respect to their maximum ordinates. This shows that if the maximum energy is a linear function of the frequency, the average energy, which is equal within the limits of experimental error to the most probable energy, also bears a linear relation to the frequency.

(3) The curves intersect the voltage axis at finite angles, both at the end which corresponds to zero energy and at the end which corresponds to the maximum energy.

(4) If the wave-length is increased to a certain value, which is in the neighbourhood of $\lambda = 27$ in the case of platinum, the distribution of velocity curve will degenerate into a straight line coincident with the current axis. The photoelectric currents in this region were too small to permit of such a curve being obtained, but the experiments show that this limiting wave-length, which we may call λ_0, has a particular meaning. It is the longest wave-length that will produce any photoelectric effect from the metal under investigation, and the electrons emitted by this light are emitted with zero velocity. This wave-length λ_0, or the equivalent frequency ν_0, is that constant which has already been alluded to which determines the photoelectric properties of the metal.

Analysis of the Distribution of Velocity Curves.

Since the curves in fig. 3 show that the mean velocity of the emitted electrons is very close to the most probable velocity, it might be thought that the mean velocity should be the characteristic velocity received by the electrons under the primary influence of the light. The deviations from the mean would then be due to collisions with other electrons in the matter traversed, some of the emitted electrons losing and others gaining energy in this way. The results can, however, be equally well interpreted on the view that all the collisions in the interior of the matter result in a diminution of the energy of the emitted electrons. We shall limit the discussion to the case of a beam of light incident normally to the emitting surface.

Let each electron which is set free from its parent atom or equivalent system in the interior under the influence of the monochromatic radiation have a constant amount of kinetic energy T_0. We shall assume that this energy diminishes to $T_0F_2(r)$ when the electron has traversed a distance r inside the matter from its point of origin, and in addition that it has to do a definite amount of work P in order to escape from the surface. The energy T of the electrons which originate at a distance r from the point where they escape from the surface is then a function of r only. It is given by

$$T = T_0F_2(r) - P. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Consider all the electrons which emerge from an element dS of the surface, and which originate at a distance between r and $r+dr$ from the point of emergence. Let θ be the angle between the radius r and the internal normal to dS. Let λ_1 be the coefficient of extinction of the light with distance. Then the number of electrons which originate in an element of volume $d\tau$ at a depth defined by r and θ will be $e^{-\lambda_1 r\cos\theta}A\,d\tau$, where A is a constant. In addition to losing energy the electrons will diminish in number with the distance traversed in the matter. Let the proportion which disappear in this way in a distance r be $1-F_1(r)$. Then the total number which reach dS and which come from a distance between r and $r+dr$ is

$$dN = \int_{-\pi/2}^{\pi/2} e^{-\lambda_1 r\cos\theta} A\,.\,2\pi r^2 \sin\theta\, dr\, F_1(r)\frac{dS\cos\theta}{r^2}\,d\theta, \quad . \quad (2)$$

$$= 2\pi A F_1(r)\,dr\,dS\int_0^1 e^{-\lambda_1 r x}\,x\,dx$$

$$= \frac{2\pi A\,dS}{\lambda_1{}^2}\,.\,\frac{F_1(r)}{r^2}\,dr\left[1-(1+\lambda_1 r)e^{-\lambda_1 r}\right]. \quad . \quad . \quad . \quad (3)$$

Also $$dT = T_0F_2{}'(r)\,dr. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus $$\frac{\partial N}{\partial T} = \frac{2\pi A\,dS}{\lambda_1{}^2 T_0}\,\frac{1}{r^2}\,\frac{F_1(r)}{F_2{}'(r)}\left[1-(1+\lambda_1 r)e^{-\lambda_1 r}\right]. \quad . \quad (5)$$

The values of T which make N a maximum are given by $\dfrac{\partial N}{\partial T}=0$, or

$$e^{-\lambda_1 r} = (1+\lambda_1 r)^{-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

On this view T is determined by r alone, and the corresponding values of T are given by solving (6) for r and substituting in (1). The maximum value of the kinetic energy of the emitted electrons is that which corresponds to $r=0$, so that when $r=0$

$$\left(\frac{\partial N}{\partial T}\right)_{r=0} = \frac{\pi A\,dS}{T_0F'_2(0)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus when T has its maximum value, $\frac{\partial N}{\partial T}$ has a finite value which is negative, since $F_2'(0)$ is negative. The value of $\frac{\partial N}{\partial T}$ when $T=0$ may be obtained by solving the equation $F_2(r)=P/T_0$ for r and substituting in (5). This value of $\frac{\partial N}{\partial T}$ is readily seen to be positive and finite, so that it is clear that the type of theory which supposes the maximum energy of the emitted electrons to be determined by the energy they receive under the influence of the light less a constant amount of work necessary for them to escape from the material is in satisfactory general agreement with the experimental results.

We shall not consider the numerical analysis of curves like those in fig. 3 in the present paper, but shall now turn to the experimental data which have been given by the other metals investigated.

Experiments with Different Metals.

Curves similar to those in fig. 2 were obtained by the same method for strips S of copper, bismuth, tin, zinc, aluminium, and magnesium, as well as platinum, using various wave-lengths of light. The curves for aluminium are represented by the full lines in fig. 2 (Pl. XIII.). The results with the other metals are shown in figs. 4, 5, 6, 7, and 8.

In each of these cases the curves for different wave-lengths reach saturation at a common point. The dotted ordinate in each figure represents the actual position of the current axis according to the reading of the voltmeter V, and the point where the dotted line meets the volt-axis is the experimental position of zero volts. But when this position of zero volts is shifted so as to correct for the contact difference of potential between the silver bulb and the metal strip used, the current-axis is shifted so as to pass exactly through the saturation-point where the curves coincide. For instance, the contact-difference of potential between silver and zinc is just 1 volt. When this is corrected for by shifting the position of zero volts to the right a distance corresponding to 1 volt, it is seen that this point, which really corresponds to zero field acting on the electrons, exactly coincides with the position where the curves reach their common maximum. This correspondence between the contact-difference of potential and the shift necessary to place the ordinate of zero volts at the saturation-point is exact, so far as we have been able to determine, in every case except that of magnesium, fig. 4. But doubtless even here the discrepancy is only apparent.

The fact that the shift required for coincidence is only 1·15 volts instead of 1·4 volts, the true contact-difference of potential between silver and magnesium, is probably due to slight oxidation of the magnesium, whereby the actual contact difference was reduced to 1·15 volts. So here, too, the shift and the contact-difference of potential probably correspond.

This point is also significant because it disproves the emission of electrons with apparent negative velocities. Since the curves reach their maxima at the ordinate which corresponds to zero volts, all the electrons possess velocities greater than zero. The occurrence of electrons with apparent negative velocities, that is to say, of electrons which are only completely liberated when there is an external electric field to draw them away from the surface of the emitting metal, has usually been supposed, in order to account for the fact that the distribution of velocity curves have often been observed to cut the axis of zero volts before reaching their maxima. Such an intersection with the current-axis is probably due either to the neglect of the effect of the contact difference of potential on the position of zero volts, or to something which prevents some of the electrons from reaching the receiving electrode unaided. Such an effect might be due to a poor vacuum, to electron reflexion, to the obstruction offered by a wire screen used in the effort to prevent reflexion, or to some peculiarity in the shape of the apparatus. Fortunately the difficulty seems to have been avoided in the form of apparatus used in this investigation.

It is now easy to understand why the values of the kinetic energies of the emitted electrons which have been published differ so widely. If the uncorrected position (the dotted line) were to be taken for the origin, it is evident that the different metals would appear to emit electrons with practically equal maximum velocities for a given wave-length, although actually those emitted by the electropositive metals possess the highest velocities.

In the case of sodium we have not been able to obtain the complete curves showing the distribution of kinetic energy. On account of the rapid photoelectric fatigue exhibited by this substance, we have only been able to determine the value of the maximum kinetic energy corresponding to different frequencies. Different methods were tried to reduce or avoid photoelectric fatigue, but they were only very partially successful. In our first experiments we cut the sodium surface in an atmosphere of hydrogen, carefully dried and purified, in a separate vessel attached to the bulb D ; so that the sodium strip could be placed in position without coming into contact with the air. But with the best care, the surface of the sodium coated over so rapidly that it gave no photoelectric current whatever. The plan finally adopted was to place a little strip of sodium in position at S, heat the bulb so as to drive off layers of adhering gas, and keep it under the highest vacuum obtainable with the Gaede pump for about 24 hours. Then the pump connexion was sealed off, and the bulb was left with a tube of phosphorus pentoxide and one of coconut charcoal immersed in liquid air for several hours more. After this a rod turning in a ground-glass joint provided with a mercury trap was turned, thus winding up a wire which drew a piece of Gillette razor-blade along so as to leave a fresh surface exposed to the light.

Even with these precautions the photoelectric sensitiveness of the sodium fell off rapidly, decreasing from a deflexion of 3000 divisions per minute to about 50 per minute in the course of two hours and a half. If photoelectric fatigue is due, as seems most probable, to the chemical effects of the surrounding atmosphere, it is clear that very minute amounts of matter can produce very sensible effects of this kind. The vacuum was unquestionably quite good in these experiments. Before applying the liquid air the pressure recorded by the McLeod gauge varied from amounts which were too small to be estimated, up to about 0·00001 mm.

As has been stated, we were not able to take the observations sufficiently quickly to obtain the complete velocity distribution curves for sodium. However, the maximum reading of the voltmeter at which any deflexion could be detected was quite easy to find. Such points correspond to the feet of the curves in Pl. XIII. fig. 2. These points were obtained as soon as possible after the sodium had been shaved and while the photoelectric currents were large, so that they should be quite accurate. In this way the following values were obtained:—

Wave-length.........	43·6	36·6	31·3	25·4	21
Apparent energy in equivalent volts...	−1·9	−1·5	−1·0	−0·2	+0·5
True energy in equivalent volts	0·6	1·0	1·5	2·3	3·0

The true values of the kinetic energy were obtained by taking the contact difference of potential between silver and sodium to be 2·5 volts. This determines the position of the maximum point in the curves like those in Pl. XIII. fig. 3.

Having thus obtained the two end points, an estimate of the mean energy can be obtained by assuming that the shape of the curves is the same as that of those given by other substances which terminate at the same points. This method was tested in a number of other cases, where all the data were known, and found to give results for the mean energy which agreed with the direct determinations. Moreover, in almost all of the very large number of cases tried the curves between the same terminal points were identical to within the limits of experimental error. The curve which showed the worst agreement with this rule is the aluminium curve for $\lambda=31{\cdot}3$, which runs across from the platinum curve at $\lambda=23$ to that at $\lambda=25$. This is shown in Pl. XIII. fig. 2. It is to be remembered, however, that a wave-length $\lambda=31{\cdot}3$ gives very small currents even with aluminium, so that the curves in this part of the diagram cannot be determined very accurately. The more typical behaviour is shown by the curves for the wave-length 21 for Pt and 25·4 for Al, which are almost identical throughout their course (Pl. XIII. fig. 2).

The Maximum and Mean Energies. Comparison with Theory.

The maximum and mean energies of the electrons emitted under the influence of light of a given frequency are readily obtained from curves like those shown in Pl. XIII. fig. 3. The maximum energy T_m, expressed in equivalent volts, is clearly equal to the intercept on the voltage axis between the point of intersection of the curves with this axis and that of the true axis of zero volts. The mean energy in the same units T_r is equal to the area which is bounded on the left by the curve, on the right by the true axis of zero volts, and below by the voltage axis, divided by the maximum current. The values of the maximum energy in this way are collected together in the following table (p. 585).

Leaving out of account for the present certain possible sources of systematic error, which will be considered more fully below, and which are likely to affect both the determinations of the mean and of the maximum energy in almost equal proportions, we are inclined to place more reliance on the measurements of the mean than on those of the maximum values. In some cases the current-voltage curves (Pl. XIII. figs. 2 & 4–8) appear to approach the voltage axis quite gradually, so that the determination of the exact point of intersection is a very difficult matter. Our electrostatic arrangements were quite sensitive and worked very satisfactorily; but the currents in this region are extremely

Metal λ_0.	λ.	T_m.	T_r.	λ/λ_0.	Metal λ_0.	λ.	T_m.	T_r.	λ/λ_0.
Na 57·7	43·6	0·60	0·30	0·755	Zn 35·7	26·5	0·92	0·52	0·740
	36·6	1·00	0·50	0·635		25·3	1·25	0·625	0·713
	31·3	1·50	0·75	0·542		23·0	1·70	0·862	0·644
	25·4	2·30	1·15	0·440		21·0	2·03	1·06	0·590
	21·0	3·00	1·50	0·365					
					Sn 33·7	26·5	0·80	0·432	0·785
Al 41·1	31·3	0·90	0·365	0·760		25·4	1·10	0·520	0·750
	27·5	1·30	0·60	0·670		23·8	1·33	0·660	0·705
	25·3	1·50	0·74	0·615		22·0	1·73	0·810	0·650
	23·0	1·90	0·965	0·560					
	20·0	2·30	1·21	0·485	Bi 33·7	25·4	0·60	0·315	0·750
						23·0	0·90	0·450	0·680
Mg 39·0	27·5	0·85	0·45	0·730		21·0	1·15	0·587	0·620
	26·4	1·02	0·585	0·705					
	25·4	1·35	0·638	0·675	Cu 30·9	26·0	0·35	0·175	0·840
	23·0	1·80	0·85	0·612		25·4	0·48	0·230	0·820
						23·0	0·73	0·335	0·745
Pt 29·1	25·0	0·51	0·266	0·870		21·0	1·02	0·475	0·680
	23·0	0·99	0·47	0·790		20·0	1·25	0·550	0·645
	21·0	1·45	0·713	0·720					

The unit for λ is $1=10^{-6}$ cm. T_m and T_r are expressed in equivalent volts.

small, and the maximum potential observed is necessarily that at which the photoelectric current is balanced by the minute back leakage which is unavoidable in an apparatus of this character, and which arises chiefly from the ionization of the air in the shielding tubes and the like. It is possible that our measurements of the maximum energy might have been improved by using a source of ultra-violet light of greater intensity, as the Heraeus quartz mercury lamp was chosen for its steadiness rather than on account of the intensity which it furnished. However, it is probable that the chief sources of error in experiments on photoelectric action arise from chemical effects at the surfaces investigated rather than from defects in the electrical and optical arrangements used.

When the foregoing values of T_m and T_r are plotted against the corresponding frequencies ν, the results for each metal exhibit a linear relation between the corresponding variables. Except in the case of copper and bismuth the lines are almost parallel to each other for all the metals. The frequencies ν_0, and the corresponding wave-lengths λ_0, which correspond to T_m and $T_r=0$, are determined by the intersection of these lines with the frequency axis. Together with the constant k, which determines the slope of the individual curves, they are collected together in the following table:—

Metal.	Values from T_m.			Values from T_r.		
	ν_0.	λ_0.	k_m.	ν_0.	λ_0.	k_r.
Na	51·5	58·3	5·2	52	57·7	2·6
Al	63	47·7	4·3	73	41·1	2·6
Mg	78·5	38·2	5·2	80	37·5	2·55
Zn	80	37·6	5·1	84	35·7	2·8
Sn	83	36·2	4·9	89	33·7	2·75
Bi	91	33	3·55	89	33·7	1·9
Cu	100	30	3·8	97	30·9	1·65
Pt	104	28·8	5·85	103	29·1	2·8

The unit for λ_0 is $1=10^{-6}$ cm. and for k_m and k_r $1=10^{-27}$ erg sec.

The values of λ_0 given by the mean energy T_r are practically identical with those given by the maximum energy T_m except in the case of aluminium. When the two differ we are inclined to attach more weight to the values from T_r for the reasons already stated.

Some years ago Einstein * showed that it followed from the unitary theory of light that the maximum energy T_m of the electrons emitted under the influence of light should satisfy the equation

$$T_m = h\nu - P, \quad \ldots\ldots \quad (8)$$

where ν is the frequency of the light, h is Planck's constant, and P the work which the electrons have to do in order to escape from the material. One of the writers † has recently shown that T_m and T_r have to satisfy the equations:—

$$T_m = h\nu - w_0, \quad \ldots\ldots \quad (9)$$

$$T_r = s(h\nu - w_0) \quad \ldots\ldots \quad (10)$$

where w_0 is the latent heat of evaporation of the electrons, per electron, at the absolute zero of temperature, and s is a quantity which depends upon the reflexion of electrons at the surface of the material. The precise definition of s is as follows. Consider the surface in question to form part of an isolated system in thermal equilibrium. It will be continually

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* *Ann. der Physik*, vol. xvii. p. 146 (1905).

† O. W. Richardson, Phys. Rev. vol. xxxiv. pp. 146, 384 (1912); Phil. Mag. vol. xxiii. p. 615 (1912); Science, vol. xxxvi. p. 57 (1912).

emitting and receiving electrons. Of the incident group some will be absorbed and others reflected. Let the proportion absorbed be α. Then the proportion reflected is $1-\alpha$. Some of the electrons in the group under consideration have greater speeds than others; so that as the proportion reflected out of any group having a given speed is a function of the speed, the proportion of the energy, in a mixed incident group, which is reflected, will be different from the proportion of the incident number which is reflected. Let β be the proportion of the energy of the group, incident in the state of thermal equilibrium, which is absorbed. Then $s=\beta/\alpha$. As the proportion of incident electrons absorbed is smaller the higher the speed, it follows that s is a positive quantity which is less than unity.

The deduction of formulæ (9) and (10) does not depend on the unitary theory of light except in so far as the unitary assumption may implicitly underlie Planck's radiation formula, or rather Wien's form

$$\mathrm{E}(\nu\theta)=\frac{8\pi}{c^3}h\nu^3 e^{-\frac{h\nu}{\mathrm{R}\theta}}, \quad . \quad . \quad . \quad . \quad (11)$$

which is used instead, as a sufficient approximation.

If we put $w_0=h\nu_0$ we have instead of (9) and (10)

$$\mathrm{T}_m=h(\nu-\nu_0), \quad \mathrm{T}_r=sh(\nu-\nu_0) \quad . \quad . \quad . \quad (12)$$

or, in wave-lengths, putting $c=\nu\lambda=\nu_0\lambda_0$

$$\lambda\mathrm{T}_m=ch\left(1-\frac{\lambda}{\lambda_0}\right), \quad \lambda\mathrm{T}_r=sch\left(1-\frac{\lambda}{\lambda_0}\right). \quad .. \quad (13)$$

A more comprehensive test of these formulæ is afforded by Pl. XIII. fig. 9, which contains all the observations which we have made. The points corresponding to the different metals are indicated thus:—

Na●, Al○, Mg∗, Zn▲, Sn+, Biʅ, Cu×, and Pt*ɪ*.

The values of λ_0 which have been used in constructing the figure are those given by plotting T_r, the mean energy, against ν. The points near the lines OB and OC represent values of T_m and those near OD and OE values of T_r. OA is the theoretical line for $\mathrm{T}_m=h(\nu-\nu_0)$ using the value of h given by radiation measurements, viz. $h=6{\cdot}55\times10^{-27}$ erg cm. Except in the case of copper and bismuth, all the values of T_m lie very near the line OB and all those of T very near the line OD. The slope of the line OB corresponds to $k_m=5{\cdot}4\times10^{-27}$ erg sec. instead of $6{\cdot}55\times10^{-27}$ erg sec.

It is thus about 20 per cent. less than the theoretical value. The slope of OD is almost exactly half of that of OB. The slope of OC is only about two thirds of that of OB, but the same relation holds between OE and OC as between OD and OB. It thus appears that s is very close to one half for all the metals investigated, even including copper and bismuth, for which the discrepancy between k_m and h is much greater than in the case of the other six metals.

The relation $T_r = sh(\nu - \nu_0)$ has only been shown theoretically to hold for the case of isotropic radiation, that is for incident radiation which is propagated with equal intensity in all directions, whereas all the values given are for light at approximately normal incidence. However, we made special experiments with platinum and aluminium to see whether rotating the strip S so as to change the angle of incidence of the light would make any alteration in the curves giving the distribution of kinetic energy. We were unable to detect any certain changes in the energy in this way, although the number of electrons emitted varied considerably. It would appear, therefore, that the difference in the distribution of energy among the electrons emitted by isotropic radiation and those emitted by radiation incident at a particular angle, is inappreciable or, at least, its determination is not a practical matter when the degree of precision which is at present attainable in experiments of this kind is taken into consideration.

The fact that all of the measured values of λT_m fall to the left of the line OA is perhaps not very surprising. Practically every source of experimental error tends to make the measured values of T_m too small. This would be the case, for example, if the surface of the strip were covered with a layer of photoelectrically inactive material such as the oxide of the metal or a layer of condensed gas or moisture; the effect of any slight leakage in the electrostatic system is also in the same direction. We are unable at present to urge any satisfactory reason why the metals copper and bismuth should appear to be in a class by themselves.

It is worth while remarking that the difference between the experimental and the theoretical relation of T_m to ν is what one would expect if there were a layer of photoelectrically inactive material at the surface of the strips which reduced the speed of the escaping electrons, provided the law of diminution of kinetic energy T with thickness x of material traversed were of the form

$$\delta T = -T f(x) \delta x. \qquad \qquad (14)$$

This makes the energy lost proportional to the initial energy for different wave-lengths, and the relation between the observed T_m and ν a linear one. The slope, measured by k_m, of the experimental line would then be less than that (h) of the theoretical line. The two lines would intersect at $T_m=0$. This is in accordance with the experimental results if the experimental values of ν_0 are really identical with the least frequencies which would cause any electrons to be emitted from a perfectly clean surface. It might be, however, that the true values of ν_0 would be less than those observed, on account of the slowest electrons being completely stopped by such a layer. In that case the relation between T and x would have to be of the form

$$T=T_0 f(x)-g(x), \quad . \quad . \quad . \quad . \quad . \quad (15)$$

when T_0 is the maximum initial energy.

There is at present, so far as we are aware, no experimental evidence bearing on the law of loss of energy with matter traversed for these slowly moving electrons, but Sir J. J. Thomson * has deduced a formula of type (14) with $f(x)=\text{constant}$, on theoretical grounds. The application of this formula can hardly be regarded as having much cogency in the present instance, but it is of some interest to see what it leads to, in the way of an estimate of the thickness of inactive matter required to produce the observed differences between theory and experiment. In the least favourable case, that of bismuth, assuming the inactive matter to be Bi_2O_3, we find $x=2{\cdot}5\times10^{-4}$ cm. In the other cases the thickness would vary down to about one-tenth of this. Thicknesses of inactive matter of this magnitude should produce distinct optical effects. The only case in which we observed visible changes of this kind was that of copper, the surface of which became darker during the experiments. The existence of photoelectric fatigue shows that the surfaces of the metals do become covered with a layer of inactive matter. Tests which we have carried out show that the change in the maximum energy and in the distribution of energy of the emitted electrons due to photoelectric fatigue is uncertain, but is certainly inappreciable in comparison with the change in the number of electrons emitted. However, a layer of inactive matter might easily have the effect of reducing the *number* of escaping electrons very considerably without causing any comparable change in the distribution of velocity among those which got through, particularly as the mode of distribution is fairly irregular to start with. It is significant that the metals for which the values of k_m show the nearest approach to the theoretical value are platinum and sodium. The former is notoriously averse to oxidation and the surfaces of the latter were cut *in situ* in the best attainable vacuum.

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* ‘Conduction of Electricity through Gases,’ 2nd edition, p. 379.

The Values of ν_0 *and* λ_0.

According to the theory which underlies formulæ (9) to (13)

$$w_0 = h\nu_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where w_0 is the latent heat of evaporation of electrons out of the material at the absolute zero of temperature. The value of w_0 can be obtained from thermoelectric data combined with the temperature variation of the rate of emission of electrons from the material when heated. The metal which has received the most extended study in this respect is platinum, and it is probable that a fairly reliable estimate of w_0 can be obtained for this material. If σ is the specific heat of electricity, one of the writers * has shown that

$$\sigma = \frac{1}{e}\left\{\frac{R}{\gamma-1} - \frac{\partial w}{\partial \theta}\right\}, \quad . \quad . \quad . \quad . \quad (17)$$

when e is the charge on an electron, R is the gas constant for one molecule, γ is the ratio of the two specific heats for the electrons, and w is their latent heat of evaporation, per electron, at temperature θ. According to Berg † the Thomson coefficient for platinum is practically constant between $-50°$ C. and $+100°$ C. and equal to $-9{\cdot}2 \times 10^2$ erg per E.M.U. per ° C. Thus from (17) w is a linear function of θ. If n is the total number of electrons emitted thermionically at θ, when the coefficient of reflexion of the electrons is neglected

$$n = A_1\theta^{\frac{1}{2}} e^{\int \frac{w}{R\theta^2} d\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where A_1 is independent of θ. Substituting the experimental numbers given by the Thomson effect, this becomes

$$n = A_2\theta^{2{\cdot}11} e^{-w_0/R\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where A_2 is independent of θ and w_0 is the value of w when $\theta = 0$.

We have applied the formula to determine w_0 from the experimental measurements of the saturation electronic currents from platinum at different temperatures, which have been made by F. Deininger*, H. A. Wilson†, and O. W. Richardson‡. These are probably the most reliable determinations which have been made, and although they are not in perfect agreement there is no reason why any one of them should be rejected. The values of w_0 in equivalent volts calculated in this way are:—Deininger, 5·03; Wilson, 5·39; Richardson, 5·61. The mean is 5·34 volts or $8{\cdot}32\times10^{-12}$ erg using $e=4{\cdot}67\times10^{-10}$ E.S.U. The value of ν_0 for platinum in the table on p. 586 is $1{\cdot}03\times10^{15}$ sec.$^{-1}$ whence

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* O. W. Richardson, Phil. Mag. vol. xxiii. p. 605 (1912).

† *Cf.* Baedeker, *Elektrische Erscheinungen in Metallischen Leitern*, p. 76.

$$h=w_0/\nu_0=8{\cdot}07\times10^{-27}\text{ erg sec.} \quad . \quad . \quad . \quad (20)$$

It will be observed that this estimate of h depends only on thermionic, thermoelectric, and photoelectric measurements, and is quite independent of the estimate $k_m=5{\cdot}85\times10^{-27}$ erg sec. Nevertheless it is very close to the radiation value $h=6{\cdot}55\times10^{-27}$ erg sec. The value (20) is, in fact, just about as much in excess of the radiation value as the other is below it.

The discrepancy between the value of h from w_0/ν_0 and from the radiation formula might be due either to w_0 being too large or ν_0 being too small. It is possible that the values of ν_0 estimated from the linear relation between T and ν are too small for some unknown reason; but it is not possible that they are sufficiently in error to account for the whole of the discrepancy. This is shown by the fact that in the case of platinum the photoelectric emission was definitely measurable at $\lambda=27$ as compared with the value $\lambda=29{\cdot}1$ deduced from the measurement of T_r. There is therefore only a possibility of an extension of λ_0 of about 2 units in this direction, and this would only account at most for about half the observed difference. As a matter of fact the tabulated values of λ_0 on p. 586, although rather higher than the wave-lengths at which photoelectric emission was observed to start, were never very far from them. Although we have made experiments in this direction with most of the substances investigated, we have not been able to satisfy ourselves that there is any certain difference between the tabulated values of λ_0 and the greatest wave-length at which photoelectric emission commences. The tests made, however, are not as delicate or reliable as might be desired, on account of the photoelectric insensitiveness of the materials in this region and of the fact that our source of light gave a line spectrum.

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* *Ann. der Physik,* vol. xxv. p. 296 (1908).

† Phil. Trans. A, vol. ccii. p. 243 (1903).

‡ Phil. Trans. A, vol. ccvii. p. xxiii. (1906).

It seems, therefore, fairly certain that part of the increased value of h deduced from (20) must be due to w_0 being too large. We think it improbable that w_0 is appreciably larger than what it pretends to be, namely, the part of the latent heat of evaporation of the thermionically emitted electrons which is independent of θ. It may be, however, that w_0 is slightly smaller for the electrons emitted photoelectrically by the complete radiation, than it is for the electrons which are emitted thermionically. If this could be established it would be important as showing that thermionic emission is something different from the photoelectric emission arising from the complete radiation characteristic of the temperature of the hot body *.

The values of ν_0 for different substances are closely related to the contact differences of potential. This is shown by the numbers in the following table, which represent the contact differences of potential between platinum and the different metals investigated :—

Metal. I.	Contact P.D. with Platinum. (Volts.)		
	Calculated. II.	Observed. III.	Calculated. IV.
Cu	·37	·13	·30
Bi	·77	·35	·64
Sn	·77	·62	·64
Zn	1·04	·90	·85
Mg	1·17	1·05	1·00
Al	1·62	1·2	1·31
Na	2·69	2·4	2·2

The observed values in column III. are the usual values, except in the case of Mg, where the observed value was ·25 volt less than that given in the standard tables. The calculated values in columns II. and IV. are derived from the corresponding values of w_0 in different ways. The differences of w_0 are taken to be equal to the differences of eV, where V is the corresponding intrinsic potential. This is in accordance with the formula

$$w_m - w_p = e\left(\mathrm{V}_m - \mathrm{V}_p - \theta\frac{\partial}{\partial\theta}(\mathrm{V}_m - \mathrm{V}_p)\right), \quad . \quad . \quad (21)$$

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* *Cf.* O. W. Richardson, Phil. Mag. vol. xxiii. p. 620 (1912).

since the term involving θ, which depends on the thermoelectric power of the metals, may be disregarded in the cases considered on account of its smallness. For similar reasons the differences of w may be taken to be the same thing as the differences of w_0.

The values in column II. were obtained by assuming that the value of w_0 for platinum was equal to that given by the thermionic measurements, viz. 5·34, in equivalent volts. A factor A was then determined so that $h\nu_0 = \mathrm{A} \times 5{\cdot}34$ where $h = 6{\cdot}55 \times 10^{-27}$ erg sec. and $\nu_0 = 1{\cdot}03 \times 10^{15}$ sec.$^{-1}$ the value of ν_0 for platinum given by the experiments. This value of A was then used as a reduction factor to determine the value of w_0 from that of $h\nu_0$ for each of the other metals. This method is equivalent to assuming that the value of w_0 is the same for the photoelectric as for the thermionic emission, and that the large value of h given by (20) is due to some unknown error in $h\nu_0$ which affects the different metals proportionately.

The values in column IV. are simply the differences of $h\nu_0$ reduced to volts per unit charge. This method of calculation is equivalent to assuming either that w_0 is in error or that it is not the same thing for photoelectric as for thermionic emission. All things considered, both II. and IV. give a fair agreement with III., although the last column agrees better than the second. On the whole, the view which puts the error in (20) on w_0 has, so far, the best of the argument.

The Frequency of Characteristic Röntgen Rays.

If the formula $\mathrm{T}_m = \nu h - w_0$ continues to apply no matter how high the frequency ν becomes, the frequency of characteristic Röntgen rays can be written down from known data. There is nothing in any derivation of the formula which would tend to confine its application to any limited range of frequency. On the other hand, its validity is closely connected with that of Planck's radiation formula, which has only been tested in the neighbourhood of the visible spectrum. The extension to the case of Röntgen rays can therefore only be regarded as speculative ; as a speculation however, it has some merit, since it is the only line of attack which seems open to us at present.

The researches of Sadler * and Beattie † have shown that when characteristic Röntgen rays fall on different substances, the energy of the emitted electrons is independent of the substance emitting them, being determined entirely by the character of the X rays. Whiddington * has shown that the maximum energy of the emitted electrons is equal to that of the slowest cathode rays which will excite the characteristic Röntgen rays. He has measured this quantity in equivalent volts in a number of cases and has shown that, in general, for Barkla's K series of X rays the energy is proportional to the square of the atomic weight of the metal of which they are characteristic. These results are consistent with the formula $T_m = h\nu_0 - w_0$ for the energy of the emitted electrons provided ν_0, the frequency of the characteristic Röntgen rays, is given by

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* Phil. Mag. vol. xix. p. 337 (1910).

† Phil. Mag. vol. xx. p. 320 (1910).

$$\nu_0 = 6{\cdot}55 \times M^2 \times 10^{14}, \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

where M is the atomic weight of the metal of which they are characteristic. This holds only for the rays which constitute Barkla's K series. The values for the L series should be given by substituting $\left(\frac{M}{2} - 25\right)$ for M in (22), to accord with Whiddington's conclusions. Thus the frequency of the Röntgen rays characteristic of copper would be, since they belong to the K series,

$$\nu_0 = 2{\cdot}64 \times 10^{18} \text{ sec.}^{-1}.$$

In the case of all these rays w_0 is negligible in comparison with $h\nu_0$. This accounts for the energy being independent of the metal of origin, as found by Sadler.

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LIV. *The* γ *Rays excited by the* β *Rays of Radium.*

By J. Chadwick, *M.Sc.*†

It has been shown by Gray ‡ that when the β rays of radium E impinge on any material they excite γ rays. The amount of the excited γ rays is large compared with the amount of primary γ rays. He has found that the excited γ rays increase in amount and in penetrating power with the atomic weight of the material on which the β rays impinge.

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* Roy. Soc. Proc. A. vol. lxxxv. p. 323 (1911); vol. lxxxvi. pp. 360, 370 (1912).

† Communicated by Prof. E. Rutherford, F.R.S.

‡ J. A. Gray, Proc. Roy. Soc. A. vol. lxxxv. p. 131, and vol. lxxxvi. p. 513.

One would naturally expect that γ rays would also be produced by the impact of the β rays of radium C, but hitherto no definite evidence of this has been obtained.

Starke[*], in 1908, showed that the amount of γ rays excited by the β rays of radium C must be very small compared with the amount of primary γ rays. He used about 6 milligrammes of radium bromide contained in a glass tube thin enough to let out most of the β rays, and measured the ionization produced by this in an electroscope. The face of the electroscope through which the γ rays passed was a plate of lead 2 cm. thick. He then placed plates of various materials just behind the radium, but found no difference in the electroscope reading. In another series of experiments the face of the electroscope consisted of thin Al foil, and the β rays were prevented from entering by means of a strong magnetic field. He again found no effect.

Davisson[†] used a slightly different arrangement. By means of a converging magnetic field he directed the β rays on to a lead plate. Any γ rays excited in the lead would have caused an increase in the ionization of an electroscope placed in a suitable position. He found some slight but uncertain evidence of the production of γ rays.

These experiments show that the amount of γ radiation excited by the β rays of radium C can at most be only 1 or 2 per cent. of the primary γ radiation.

It is of importance to settle definitely whether the β rays of radium C excite γ rays or not, and to find the amount of excited radiation under definite conditions compared with the primary radiation. It is evident, from the above experiments, that if the excitation of γ rays is to be shown quite clearly, a method must be used which will increase the apparent proportion of excited γ rays to primary γ rays. This has been done by means of the arrangement shown in the figure (p. 596).

A quantity of radium emanation contained in a very thin glass tube is placed at E between the polepieces of a large electromagnet. A converging magnetic field is obtained by using polepieces of suitable shapes.

Before the primary γ rays can enter the ionization chamber A they have to pass through the lead screen L, which absorbs about 95 per cent. of the rays.

The converging magnetic field concentrates about one half of the total number of β rays from the emanation tube on to a plate of any given material placed at P. The plates used were about $3\frac{1}{2}$ cm. square and sufficiently thick to stop all β rays.

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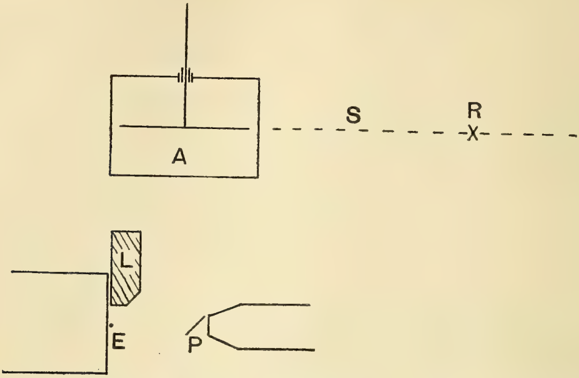
[*] H. Starke, *Le Radium*, Feb. 1908, p. 35.

[†] Davisson, Phys. Rev. vol. xxviii. p. 469 (1909).



The ionization in the chamber A was measured by a modified form of the balance method of Rutherford and Chadwick[*]. The ionization current in A due to the γ rays was balanced against an equal and opposite ionization current due to a film of uranium oxide. As it was impossible to move either the emanation tube and magnet, &c., or the ionization chamber, it was arranged that the current due to the γ rays from the source E was less than that due to the uranium source, and a balance was obtained by adjusting the position of a radium tube R along the scale S.

The method of observation was as follows:—A plate of any material was placed at P and the position of the radium R adjusted till a balance was obtained. The magnetic field was then excited, and it was found that to obtain a balance the distance of the radium from A must be increased. In the majority of the experiments the change in the balance position corresponded to a change of about 20 per cent. of the ionization due to R, that is, the ionization produced in A by the excited γ rays from P was one-fifth of the ionization due to R when in the first position.

It has been shown in a previous paper that the intensity of the γ rays from a radium-source at a distance r is very nearly proportional to $\frac{e^{-\mu r}}{r^2}$, where μ is the coefficient of absorption of the γ rays by the air.

If r_1 is the distance from the centre of A of the position of balance of the radium R without the magnetic field, r_2 the corresponding distance with the magnetic field, then the magnitude of the excited γ ray effect is proportional to $\frac{e^{-\mu r_1}}{r_1^2} - \frac{e^{-\mu r_2}}{r_2^2}$.

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[*] Rutherford & Chadwick, Proc. Phys. Soc. April, 1912.

The distance r_1 was always made about 90 cm., and the difference between r_1 and r_2 was never more than 10 cm. It was therefore sufficient to calculate the magnitude of the effect as above, using the distance of the balance position from the centre of A, without taking into account the shape or dimensions of the ionization chamber.

In this way the amounts of γ radiation excited in a few materials were measured, the face of the ionization chamber being a lead plate 1·7 mm. thick. The amount of excited radiation from a plate of metallic uranium, containing about 87 per cent. of uranium, is taken as 100.

The balance was adjusted to an accuracy of about 1 part in 300, and therefore the measurements of the amount of excited radiation could be made with an accuracy of 3 or 4 per cent. It was therefore possible to determine approximately the absorption coefficients of the γ rays excited in different materials. Iron was used as the absorbing substance, as plates of the necessary thickness were readily obtainable, and because it does not cut out the softer radiations too rapidly.

The amount of excited radiation was first measured when A was covered with the lead plate only, and then with the addition of an iron plate 1·3 cm. thick. The absorption in this plate gives the absorption coefficient μ_1 within the range from 0 to 1·3 cm.

A further iron plate of the same thickness was then placed over the chamber, and the amounts of excited radiation again measured. The absorption in this second plate gives the absorption coefficient μ_2, within a range from 1·3 cm. to 2·6 cm. of iron. The results are given in the following table:—

Material.	Relative amount of excited rays.	$\mu_1\,(\text{cm.})^{-1}$.	$\mu_2\,(\text{cm.})^{-2}$.
Uranium	100	1·2	·8
Lead	92	1·3	·8
Tin	82	1·4	·9
Zinc	79	1·5	·95
Aluminium	75	1·8	1·0

It will be seen that the amount of excited radiation decreases with the atomic weight of the material. The radiation also becomes softer the lower the atomic weight. The differences between the various elements are, however, not so great as those observed by Gray when the β rays of radium E are used as the exciting rays. The numbers in the second column represent the energy spent by the excited γ rays in the chamber A, and not the total energy of the rays. Since the softer rays will spend a greater proportion of their energy in A than the harder rays, the differences between the various materials are really greater than the numbers indicate.

The large difference between the values of μ_1 and μ_2 indicates that the excited γ rays differ widely in penetrating power. The absorption coefficients of the primary γ rays were measured under identical conditions, and were found to be $\mu_1 = \cdot340$ cm.$^{-1}$ and $\mu_2 = \cdot314$ cm.$^{-1}$. Thus the excited rays are, on the whole, much softer than the primary rays, although the rapid diminution in the absorption coefficient would show that a small proportion of the excited rays is probably as penetrating as the primary rays. The absorption coefficients could not be found through greater thicknesses as the effect to be measured was too small.

The above experiments were repeated, using a plate of aluminium 1 cm. thick in place of the lead plate, but the results obtained were practically the same.

Soddy and Russell* have found that the γ ray activity of a preparation of uranium X of the same β ray activity as a preparation of radium C gave only 2 per cent. of the amount of γ radiation of the latter. Their preparation of UrX was deposited on a piece of platinum. It is shown below that the total amount of γ radiation excited by the β rays of RaC when they fall on uranium metal is about 0·3 per cent. of the primary radiation. The amount of excited γ radiation from platinum will be a little less than this. As the β rays of uranium X are of about the same average velocity as the average β ray of radium C, one would expect them to excite about the same amount of γ radiation. Since in the experiments of Soddy and Russell only one half of the β rays fall on the platinum, it is seen that not more than 10 per cent. of the total γ radiation of uranium X observed by them can be due to the impact of the β rays on the platinum. The remainder must arise from the transformation of the atoms of uranium X. It might be expected that the primary γ rays of uranium X would be of similar penetrating power to the excited γ rays of uranium. Unfortunately the absorption coefficient of the γ rays of uranium X has not been measured over the range used above. Soddy and Russell found an absorption coefficient in iron of ·34 cm.^{-1} within a range of 2·52 cm. to 7·57 cm., but their results indicate a much higher coefficient over the first 2 cm.

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* Soddy & Russell, Phil. Mag. Oct. 1909.

The ratio of the amount of the excited γ radiation to the primary γ radiation from the emanation was determined in the following way. The lead screen L was taken away, and the current in A due only to the emanation tube E was determined. This was 26·9 divs. per sec. The current due to the radium R, when in its usual position, was then measured. This was ·43 div. per sec. Thus the ionization due to the unabsorbed primary rays was 63 times the ionization due to the radium R. Now the amount of excited γ radiation from uranium metal, referred to the same time, was 10 per cent. of the radiation from R, measured by the ionization produced in A. Hence the γ radiation excited when the β rays fall on uranium is about 0·16 per cent. of the primary γ radiation. This is produced by the β rays which are concentrated on P by the direct action of the magnetic field, together with those which are first reflected by the iron polepiece. According to McClelland and Schmidt (see *Jahrbuch der Radioaktivität*, 1908) iron reflects from 30 to 40 per cent. of the β rays falling on it. Thus about 60 or 65 per cent. of the total number of β rays are directed on to the plate P. Hence, assuming that the excited γ rays are given out equally in all directions, the amount of excited γ radiation from uranium metal due to the total number of β rays is about 0·3 per cent. of the primary γ radiation. It is thus not surprising that the earlier observers were unable to detect the γ rays excited by the β rays of radium C.

The proportion of β rays directed on to the plate P can be calculated when the magnetic field is known. For the present purpose it is sufficient to consider the magnetic field as due to a single magnetic pole, the position and strength of the pole being given by the intensities of magnetic field at the polepieces. These were 1700 gauss at the broad polepiece and 3050 at the small one. The distance between the polepieces was 7·6 cm. From this it can be found that β rays of all velocities up to $2\ 9 \times 10^{10} \frac{\text{cm.}}{\text{sec.}}$ strike the plate P.

An attempt was made to observe the γ rays excited by β rays of a definite velocity. Danysz[*] gives two groups of β rays having velocities $2{\cdot}85 \times 10^{10} \frac{\text{cm.}}{\text{sec.}}$ and $2{\cdot}87 \times 10^{10} \frac{\text{cm.}}{\text{sec.}}$.

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[*] Danysz, *Le Radium*, Jan. 1912.

The first group has a fair photographic action, the second a strong action. Taking into consideration the intensity of their photographic action and the variation of ionization with velocity, these two groups should contain a relatively large number of β rays. Consequently, a magnetic field was used which would direct all β rays of velocity less than $2\cdot 8\times 10^{10}\frac{\text{cm.}}{\text{sec.}}$ on to the plate P, and a balance obtained. Then the usual field was excited, and a balance again obtained. Some slight but rather uncertain evidence of the excitation of γ rays was obtained, but the decay of the emanation during the course of the observations made measurement of such small effects very difficult. Even had a constant source of β rays been available, the difference in amount of excited γ radiation was too small to measure with certainty.

If it be supposed that the γ rays from radioactive matter are produced by the β rays, these experiments bring out clearly the high efficiency of the transformation of β rays into γ rays during the disintegration of the atom of radium C compared with the efficiency of the conversion of β rays into γ rays when the former fall on matter of high atomic weight. As Gray has shown, the exact converse holds for the product radium E.

Similar experiments have been made, using emanation contained in a glass tube sufficiently thin to let out the α rays, and it has been found that a measurable amount of γ rays is apparently produced by the impact of α rays. The discussion of these experiments is reserved for a later paper.

I desire to express my best thanks to Prof. Rutherford for suggesting this research, and for his help and interest throughout the course of the experiments.

LV. *The Gudermannian Complement and Imaginary Geometry.* *By* GEORGE F. BECKER*.

IN applications of the gudermannian to physical problems, it is in many cases convenient to employ the complement of this angle rather than the angle itself. This slight modification also helps to bring out interesting analogies.

Let the gudermannian complement be denoted by

$$G(u)=\pi/2-\operatorname{gd}u\,;$$

then the familiar relations between the gudermannian and hyperbolic functions become

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* Communicated by the Author.

$$\cot G(u) = \sinh u,$$

$$1/\sin G(u) = \cosh u,$$

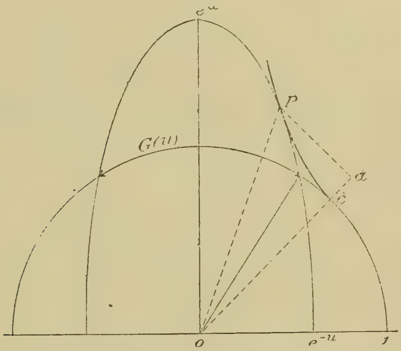
$$\cos G(u) = \tanh u,$$

$$\tan\left[\frac{\pi}{4} - \tfrac{1}{2}G(u)\right] = \frac{1 - \sin G(u)}{\cos G(u)} = \tanh\frac{u}{2},$$

$$\cot\tfrac{1}{2}G(u) = e^u.$$

The gudermannian complement is not a recondite function useful only on rare occasions, but one of the simplest and most useful of all functions. For instance, in an ellipse, let a mean proportional between the axes be selected as the unit of length, and about the centre of the ellipse let a unit circle be described as in fig. 1. The area of this circle and of the ellipse will be equal, and for that reason it has been suggested that the diameters passing through the intersections of the two curves should be called isocyclic diameters*. The acute angle between these diameters is $G(u)$, the axes are e^u and e^{-u}, or $\cot\frac{1}{2}G(u)$ and $\tan\frac{1}{2}G(u)$; the tangent of the angle which either isocyclic diameter makes with the major axis is also e^{-u}, and the square of the focal distance is $2\cot G(2u) = 2\sinh(2u)$. In short, the gudermannian complement specifies the ellipse more succinctly than does either the eccentricity or the ellipticity, and ought to be introduced into the elementary geometry of that curve.

Fig. 1.



Area $ocP = u/2$; $oa = \cosh u$; $aP = \sinh u$.

If the ellipse is regarded as derived by finite strain from the circle whose radius is the geometric mean of the axes, this function has still other luminous properties. In a pure shear the particles which in the unstrained state lie along a radius at 45° to the axes lie after strain along the isocyclic diameter, this material line having described an angle $\pi/4-\frac{1}{2}\mathrm{G}(u)$. This same radius during strain sweeps over an area $u/2$ which is an hyperbolic sector. In scission (slide, shearing motion) the angle of rotation is $90°-\mathrm{G}(u)$, and one isocyclic diameter remains stationary while the other sweeps an area u. The amount of shear is $2\cot \mathrm{G}(u)$.

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* Smithsonian Math. Tables, p. xxxi.

Since all deformations can be resolved into pure shears and scissions, all deformations can be reduced to terms of the gudermannian complement, and no simpler treatment has yet been suggested *.

Consider an ellipsoid of three distinct axes $h\alpha$, $h\beta$, $h\gamma$. This may be regarded as the strain ellipsoid derived from a sphere of radius $(\alpha\beta\gamma)^{1/3}$ by a dilatation of ratio h, and by distortion. It is evidently legitimate to take this radius as unity, so that $\alpha\beta\gamma=1$. The volume of the strain ellipsoid is then $\frac{4}{3}\pi h^3$, and for no strain $h=1$. Let $\alpha>\beta>\gamma$ and consider the ratios of the axes, $h\alpha/h\beta$, $h\beta/h\gamma$, $h\alpha/h\gamma$. These are all greater than unity if there is any strain at all. Hence they may be represented by hyperbolic cosines, thus

$$\frac{h\alpha}{h\beta}=\cosh a;\quad \frac{h\beta}{h\alpha}=\cosh b;\quad \frac{h\alpha}{h\gamma}=\cosh c,$$

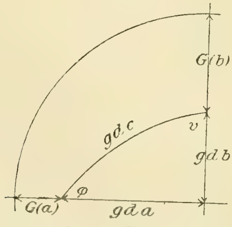
and here $$\cosh a\,.\cosh b=\cosh c.$$

If the gudermannian is substituted in this equation,

$$\cos \mathrm{gd}\, a \cos \mathrm{gd}\, b=\cos \mathrm{gd}\, c,$$

showing at once that the three angles are those subtending the sides of a right-angled spherical triangle as shown in fig. 2. The angles opposite gd a and gd b are marked respectively v and ϕ, but the complements of these angles are

Fig. 2.



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* See Smithsonian Math. Tables, introduction; and Bull. Geol. Soc. Amer. vol. iv. 1893, p. 13.

more interesting than the angles themselves. Putting $A = 90° - \phi$ and $B = 90° - \upsilon$, it appears at once that

$$\tan A = \frac{\tanh a}{\sinh b} = \frac{\cos G(a)}{\cot G(b)},$$

$$\tan B = \frac{\tanh b}{\sinh a} = \frac{\cos G(b)}{\cot G(a)}.$$

Here it is known that A is the angle which the circular section of the strain ellipsoid under discussion makes with its greatest axis*, and it is evident that B may be considered as the angle made by the circular section of a second ellipsoid with its greatest axis. The axes of this second ellipsoid are $1/h\alpha$, $1/h\beta$, $1/h\gamma$; in other words, it is the reciprocal of the first. A and B are each in general less than $\pi/4$, a value which they reach only for vanishing strain.

A very close relation exists between a strain ellipsoid and its reciprocal. This is most readily seen in the case of a mass subjected only to finite, homogeneous deformation, which can always be represented by two shears of ratio α and β. If these two shears have their axes of extension in common they deform the sphere into an ellipsoid whose axes are $\alpha\beta$, $1/\alpha$, $1/\beta$. If the same two shears are combined by their contractile axes, they yield an ellipsoid whose axes are $1/\alpha\beta$, α, and β. This second ellipsoid is thus the reciprocal of the first. The loads (or initial stresses, or stresses into areas) are the same in absolute value in the two cases, but with signs reversed; so that equal finite loads of opposite signs produce deformations of reciprocal ratios.

A shear results from the action of two loads, Q and P, at right angles to one another if $P = -Q$. Q acting by itself would produce a dilatation of ratio say h_1, and P a cubical contraction of ratio say $1/h_2$. Acting together to produce a shear they must give a dilatation $h = h_1/h_2$. But since a shear is undilatational, $h = 1$. Therefore equal forces of opposite signs produce not merely deformations but strains of reciprocal ratios.

Hence an elastic, homogeneous sphere subjected to a finite homogeneous strain and then allowed to vibrate is converted into the reciprocal ellipsoid at the opposite phase. This vibration is not harmonic; it becomes harmonic, however, for infinitesimal amplitudes *.

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* Smithsonian Math. Tables, p. xxxii.

Thus the angles A and B are of interest in the dynamics of a vibrating elastic mass.

Interesting also are the planes of maximum tangential strain or maximum slide. In the general ellipsoid there are four sets of such planes; two of these are symmetrically placed with reference to the greatest axis, make equal acute angles with it, and are perpendicular to the plane of the greatest and least axes. The other two are symmetrical with reference to the intermediate axis with which they make acute angles, and their directrices lie in the plane of this and the least axis. The strain along the first pair of planes is maximax and along the second pair minimax.

The angles which these planes make with the axes are dependent wholly on pure deformation, and are independent of dilatational stresses or pure rotation. They are thus reducible to terms of pure shear. Any number of pure axial

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* The finite elastic load-strain function, whatever it is, must fulfil the reciprocal conditions set forth above. It is manifest that they would be satisfied by the hypothesis

$$\alpha = e^{Q/6n}, \quad h = e^{Q/9k}, \quad \alpha^2 h = e^{Q/M},$$

where n is the modulus of rigidity, k the modulus of cubical dilatation, and M Young's modulus. To the best of my knowledge, I long since proved that only this hypothesis will satisfy the conditions (Amer. Journ. Sci. vol. xlvi. 1893, p. 337). Finite strain, however, seems to excite almost no interest, and, so far as I know, the only authority who has discussed my conclusions is Ostwald, who approved them (*Zeitsch. Phys. Chemie*, vol. xiii. 1894, p. 136). These functions can, of course, be expressed in terms of the gudermannian complement, or, in other words, u may be regarded as a load expressed in terms of an appropriate modulus.

The hypothesis leads to the inference that Poisson's ratio

$$\sigma = \frac{-dx}{x} \bigg/ \frac{dy}{y}$$

is constant, irrespective of the state of elastic strain. Here $x/x_0 = h/\alpha$ and $y/y_0 = \alpha^2 h$. By integration it follows that the equation of continuity is $xy^\sigma = x_0 y_0{}^\sigma$, which is unquestionably true for the three cases $\sigma = 1/2$, $\sigma = 0$, and $\sigma = -1$. Of these the first is nearly realized by indiarubber and the second by cork. The case of an infinitely rigid but compressible mass is given by $\sigma = -1$ or, what amounts to the same thing, the case of a real mass subjected only to hydrostatic pressure.

Only on this hypothesis will the frequency of vibrations be independent of their amplitude.

For small strains let $\alpha^2 h - 1 = f$, then

$$f = Q/M + \ldots.$$

which is Hooke's law, and my results do not conflict in any way with those of the classical investigations of elasticity, which, however, they tend to simplify shears of finite amount are reducible to two lying in planes at right angles to one another having one axis in common, and neither produces any relative tangential motion or slide in the plane of the other. In a pure shear of ratio $\alpha = e^u$ the planes of maximum tangential strain stand at an angle to the major axis of $\frac{1}{2}\mathrm{G}(u) = \cot^{-1}\alpha$. For this case they are circular sections of the shear ellipsoid, and in them lie the isocyclic diameters. If a shear of ratio γ, at right angles to the plane of α, $1/\alpha$, is superposed on this strain, then the sheets of particles subject to maximum tangential strain by the first shear are deflected into a new position, and now make an angle ω with the axis α. It has been shown and is easily seen that

$$\tan\omega = \frac{1}{\alpha\gamma} = \beta.$$

If the γ-shear had been applied first there would have been maximum slide at $\cot^{-1}\gamma$, and this by the α-shear would be reduced to $\cot^{-1}(\gamma\,.\,\alpha)$. Thus each of the four sets of planes of maximum tangential strain makes with the least axis an angle $\pi/2 - \omega$.

In finite extensions as well as in infinitesimal ones a tensile load Q is divisible into thirds, of which one produces dilatation and each of the others a shear. From two of Cauchy's stress quadrics it may be shown that the load on any central plane of the shear ellipsoid is the same or Q/3. On planes whose directrices are the principal axes this load is normal. There are two other planes on which it is wholly tangential, and these make with the greatest axis an angle whose cotangent is the ratio of shear. In other words, they are planes of maximum slide as well as of maximum tangential load. Maximum tangential stress, on the other hand, occurs at 45° to the axis of stress for any homogeneous strain, and on planes at this angle the slide falls short of a maximum.

Many substances, like mild steel, if ruptured by tension, part along surfaces which make angles with the axis of stress not very different from 45°, and most homogeneous substances ruptured by pressure break at similar angles to the axis of stress. The fragments into which rupture divides a specimen must show at least a little elastic recovery, which in the case of tensile loads would increase the apparent angle of planes of parting to the axis of stress, and in the case of rupture by pressure would decrease these angles. Hence, if rupture actually occurred on planes at 45° to the axis, the specimens broken by tension would show surfaces inclined to the direction of force by somewhat more than 45°, and specimens broken by pressure would have faces at less than 45° to the axis. As a matter of fact, rupture at sensibly 45° occurs only in brittle substances such as glass, which break when the deformation is extremely small. The scrap-heap of any testing shop shows that mild steel and similar materials under tension part on surfaces standing at less (instead of more) than 45° to the direction of stress, and that crushing produces partings at more (instead of less) than 45° to this direction. Prof. J. A. Ewing has summarized the experimental data as showing that the partings in crushed cast iron stand at about 55° to the axis of stress, and those in steel under tension at about 25° to this axis, pointing out that these substances distinctly do not yield on planes of maximum tangential stress [*]. Observations of my own on rocks, colloids, and pseudosolids as well as on metals show similar relations. The actual partings vary from 45° in the same sense as do the planes of maximum tangential strain, and vary with the plasticity of the material in the same sense as does the position of these planes.

Everything known to me is consistent with the theory that not merely the ruptures produced in most materials by testing-machines take place on planes of maximum slide or load, but also the joints, faults, and slaty cleavage of rocks [†].

For geophysical purposes it is thus vital to find tan ω or β

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[*] Enc. Brit. 11th ed. vol. xxv. p. 1016.

[†] Although indiarubber is a substance with very anomalous elastic properties, it seems to me that the behaviour of various preparations of rubber affords valuable suggestions. Thus an ordinary rubber band, made of raw rubber with some 10 per cent. of sulphur and vulcanized, may be stretched to about 8 times its length, but beyond this point is almost as inextensible as a bit of twine. For the buffers of railway carriages and similar purposes rubber is mixed with something like 35 per cent. of mineral matter for the express purpose of limiting the deformation of which it is capable. This addition changes the Young's modulus, as it evidently must, and it is also clear that a block of such rubber cannot yield to pressure elastically beyond the point at which the mineral particles are forced nearly into contact. Although the elastic limit is much reduced by the addition of mineral matter, the elasticity is not materially impaired; for such springs often do duty for a considerable number of years. Now a real elastic solid might be conceived as a mixture of particles almost incapable of deformation with a substance ideally elastic or capable of indefinite stretching and dilatation. Such a mixture would have a definite and possibly small elastic limit, but would be perfectly elastic within this limit. Above the elastic limit it must either break or yield through a permanent readjustment in the distribution of the contained inelastic particles which might be conceived as of molecular dimensions.

in terms of the other functions*. Now

$$\beta^3 = \frac{\beta^2}{\alpha\gamma} = \frac{\cosh b}{\cosh a} = \frac{\sin (2\mathrm{B})}{\sin (2\mathrm{A})} = \frac{\sin \mathrm{G}(a)}{\sin \mathrm{G}(b)},$$

and thus the angle B is a significant feature of the strain ellipsoid itself, as well as of the reciprocal ellipsoid.

It is noteworthy that in the simple case of pure deformation discussed the circular functions give the relative positions of points in the mass to one another, while the hyperbolic functions appertain to the lines of flow or to the absolute motions of the particles. This distinction is not preserved, however, in the case of rotational strains.

Having thus outlined the parts played in finite homogeneous strain, flow, and rupture of rocks and other solids by the gudermannian complement and the angles A and B, it may be well to write down for reference a few of the formulæ connecting these functions :—

$$\sin \mathrm{A} = \frac{\cot \mathrm{G}(a)}{\cot \mathrm{G}(c)} = \frac{\sinh a}{\sinh c}.$$

$$\cos \mathrm{A} = \frac{\cos \mathrm{G}(b)}{\cos \mathrm{G}(c)} = \frac{\tanh b}{\tanh c}.$$

$$\cos \mathrm{A} = \frac{\sin \mathrm{B}}{\sin \mathrm{G}(a)} = \sin \mathrm{B} \cosh a.$$

$$\cot \mathrm{A} = \frac{\cot \mathrm{G}(b)}{\cos \mathrm{G}(a)} = \frac{\sinh b}{\tanh a}.$$

$$\cos \mathrm{B} = \frac{\cos \mathrm{G}(a)}{\cos \mathrm{G}(c)} = \frac{\tanh a}{\tanh c}.$$

$$\cos \mathrm{B} = \frac{\sin \mathrm{A}}{\sin \mathrm{G}(b)} = \sin \mathrm{A} \cosh b.$$

$$\sin \mathrm{B} = \frac{\cot \mathrm{G}(b)}{\cot \mathrm{G}(c)} = \frac{\sinh b}{\sinh c}.$$

$$\cot \mathrm{B} = \frac{\cot \mathrm{G}(a)}{\cos \mathrm{G}(b)} = \frac{\sinh a}{\tanh b}.$$

$$\tan \mathrm{A} \text{ and } \mathrm{B} = \sin \mathrm{G}(c) = \sin \mathrm{G}(a) \sin \mathrm{G}(b).$$
$$= \operatorname{sech} c = \operatorname{sech} a \operatorname{sech} b.$$

$$\mathrm{A} + \mathrm{B} < \pi/2.$$

Many readers will perceive at a glance that these are

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[*] Bull. Geol. Soc. America, vol. iv. 1893, p. 13; and Amer. Journ. Sci. vol. xxiv. 1907, p. 1.

neither more nor less than the standard formulæ of Lobachevsky's imaginary or hyperbolic geometry for right-angled triangles, the negative curvature being taken at unity. The only difference is that for $\Pi(u)$ I have used $G(u)$.

Whether space has negative curvature or not*, Lobachevsky's functions are applicable to physical relations so familiar as to be commonplace, and for this purpose they are more advantageous than any others yet devised.

In physical questions the gudermannian complement should be employed for the most part rather than the gudermannian, and these functions deserve to be introduced into elementary mathematics †.

Since Lobachevsky's $\Pi(u)$ is equivalent to the gudermannian complement, a table of the gudermannian such as that in 'Smithsonian Mathematical Tables' becomes a table of $\Pi(u)$ by the simple process of subtracting the tabulated values from $\pi/2$, and this opens the way to the employment of these functions in fields other than that of geology, notably in electricity.

Washington, D.C.,
May 24, 1912.

LVI. *On Potential Measurements in the Neighbourhood of the Electrodes in Point-plane Discharge. By* Miss P. M. Borthwick, *B.Sc.*‡

IN a paper on the ionizing processes at the surface of a point discharging in air (Phil. Mag. Aug. 1910), it was shown by Drs. Chattock and Tyndall that the value of the field at the surface of a discharging point, under various conditions, could be obtained by measuring the pull of the lines of force on its end, which was made hemispherical for the purpose. These field measurements were made by them, and by Dr. Tyndall, for varying values of current, distance, and size of point, both when the point was opposite a plate and when it was subjected to a stream of ions arriving at its end from an external source. These ions were of opposite sign to that of the point and are referred to below as "external ions."

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* If the entity in which the properties of æther inhere is ponderable, the æther must be confined to the portions of space characterized by stellar bodies, the æther must be in a state of strain, and the path of light is not rectilinear for Euclidian space.

† For elementary work "deformation angle" might perhaps be a better term than gudermannian complement.

‡ Communicated by Dr. A. M. Tyndall.

The following were the main results obtained :—

The field at the surface of a point discharging on to a plate is independent of the distance between the electrodes and, for a positive point, is independent of the current. For a negative point, the field seems to decrease with increase in current, but it was pointed out that it is doubtful whether the pull method may be applied with so much accuracy in the case of negative discharge. The value of the field at a negative point was somewhat greater with small currents, and somewhat less with large currents, than at a positive point. Negative ions supplied from an external source decreased the discharging field at the surface of a positive point, while positive external ions had no effect upon that at a negative point, except when the source (which was another discharging point) was placed close to it. Theoretical explanations of these results were suggested.

The work described below was undertaken mainly with the view of obtaining support for these results, by measurement of the potential drop in the neighbourhood of a discharging point.

Method.

If the potential slope between a point and a plane is mapped by means of an exploring wire, then, assuming that the wire itself introduces no disturbance of the field and that it takes up the true potential of the air at its surface, the distribution of field is directly obtained.

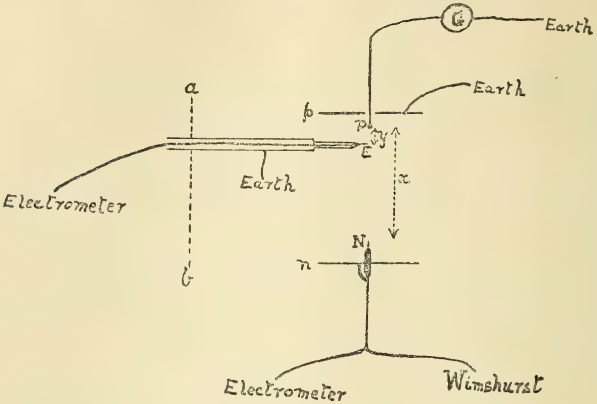
The experiments, which were carried out in open air, may be divided into two groups, viz., Investigations of field (1) near the point, (2) near the plate.

With regard to (1), there seemed to be no doubt whatever that the exploring wire would introduce considerable disturbance of the field and that quantitive readings would be unattainable. Such disturbance being present, however, in both signs of discharge, it was felt that some qualitative results might be obtained, particularly with regard to the comparison of the effects of positive and negative discharge. It will be shown that some interesting conclusions have been reached, which are, in the main, consistent with those previously deduced from the work already mentioned.

The investigation of the field near the plate was carried out for certain special ranges of current and distance between electrodes, upon which some information was required.

Fig. 1 shows the arrangement of the apparatus.

Fig. 1.



In experiments (1), the discharge point P was earthed through a high resistance galvanometer, the plate *p*, insulated from P, being earthed directly. The point N, of much smaller diameter than P, supplied external ions to P of opposite sign to that of P, and was connected, together with the plate *n*, to a wimshurst. N could be drawn down below plate *n* if desired, in which case ordinary point-plane discharge occurred. The distance between the electrodes (x) could be varied at will. In experiments (2) N was removed, P was connected to the wimshurst, and the opposite plate (of polished brass and diameter 15 cm.) was earthed through the galvanometer.

The exploring point E was of finest platinum wire (50 G) and protruded about 1 mm. from a fine quartz sheath made, however, sufficiently thick to be rigid under the existing electrostatic forces. It was connected to a previously calibrated Braun electrometer by a wire sheathed in insulation, the outer surface of which was earthed. The explorer was movable along the vertical line $a\,b$. A second Braun electrometer was used to measure the difference of potential between the electrodes when required.

Results.

Potential readings near the point.—Owing to the disturbing influence of E it was impossible to obtain accurate readings within about 3 mm. of P, since it was found that in this region the potential difference between the point P and the plate, for a constant current, increased rapidly as E approached P. There was a further effect which unfortunately limited the possibility of obtaining quantitative results, viz., the passage of sparks between P and E at short distances. The critical distance for this effect decreased with decrease in size of P, and by making P very small, readings could have been taken within a few tenths of a millimetre of its surface. In this case, however, the disturbing influence of E would have been so great that even comparative results of positive and negative discharge would not have been reliable.

The main work was therefore done with P=0·36 mm. diameter, and E fixed at 2 mm. from P.

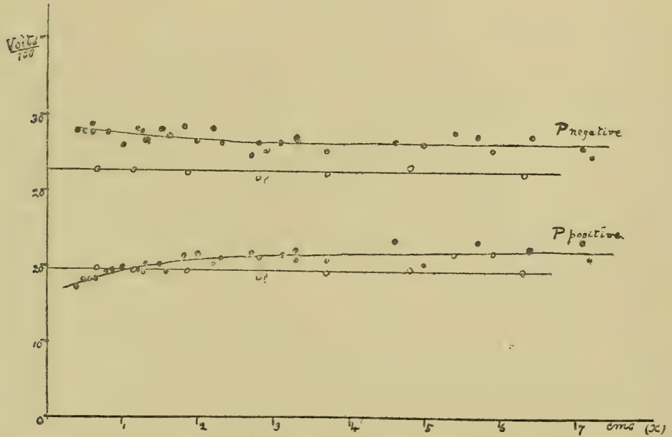
The results may be divided into two groups (a) and (b).

(a) *No external ions supplied.*—For this N was withdrawn, leaving a plate opposite P.

By taking the potential of E with various currents for a given value of x, and extrapolating to zero current, the potential drop (V_0) close to the point, when the latter was about to discharge, was obtained. Various sets of these readings were taken, corresponding to different values of x, ranging from $x=0·6$ cm. to $x=6·3$ cm.

Curves I. (open circles) show V_0 plotted with x. The curve for P− is drawn to the same scale as that for P+, but is displaced along the V axis, for convenience. The mean values of V_0+ and V_0- are 1980 and 2270 volts respectively.

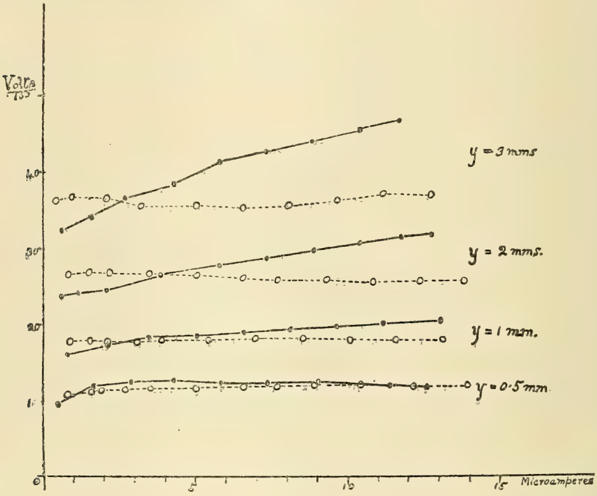
Curves I.



It will be seen that, for both positive and negative discharge, V_0 is constant for all values of x. This result is consistent with the measurements, by the pull method, of the field *at* the surface of the point under the same conditions, and proves conclusively that although the minimum discharging potential between a point and a plane depends on the distance between the electrodes, the potential drop in the neighbourhood of the point does not.

The readings, for any given value of x, of the potential drop (V) for different currents (C) are interesting, and are shown in Curves II., which include V, C curves for different

Curves II.



distances (y) between the point P and the explorer E, and for both positive (full lines) and negative (broken lines) discharge from P. (N.B. The curves for $y=2$ mm. and $y=3$ mm. are displaced along the V axis for convenience, the ordinates having been multiplied by 1·25 and 1·5 respectively.) It will be seen that for a given value of y, V is practically constant for all currents for a negative point; for a positive point, except for the smallest value of y, V increases with increase in current.

Now when the current is passing, V is complex in character, being made up of the potential drop *at* the point (anode or cathode as it may be), the potential drop in the glow, and that in the space between the glow and E. This being so, it is not surprising that V changes with current. But the rate of change decreases as y decreases, and readings taken with $y=0·5$ mm. show that, at the shortest distance of E from P, the variation with current has disappeared. It was, therefore, evidently an effect due to the space between the glow and E.

The fact that the variation does not occur for negative discharge may result from two possible causes:—(1) That the glow, with its accompanying wholesale ionization, extends further from a negative point than from a positive; this is indicated by the fact that the glow seen on a negative point when examined through a microscope is trumpet-shaped, whilst the positive glow appears as a velvety layer. (2) That the space between the glow and E is filled, in the case of positive discharge, with slow moving + ions, and in the case of negative, with the faster — ions. Eliminating this region, the potential drop near P for positive discharge, as well as for negative, is thus shown to be independent of current. This, again, is consistent with the results of "pull" determinations of the field at the surface of the point.

The influence of the sign of the point on the potential drop necessary to start discharge is small, though the value for P — appears to be consistently a little greater than that for P +. This result is also in agreement with the measurements of the field under the same conditions by the pull method.

(b) *External ions supplied.*—To study the effect of supplying to P ions of a given sign from an external source, N was introduced (fig. 1). P was viewed, in the dark, through a microscope, and the current from N was adjusted to a value just sufficient to cause P to discharge (as indicated by the appearance of a glow). Readings of this current and the corresponding potential of E were taken for different values of x. The potential drop (V_0) between P and E, at the instant of discharge from P, was thus obtained, and is shown plotted with x in Curves I. (filled circles), for positive and negative discharge from P. A comparison of these with the curves obtained with no supply of external ions (open circles) shows that (except for small values of x, in which case the readings were unreliable because the three points P, N, and E were all so close together) the drop in potential near P, for both P + and P —, is increased by supplying external ions of the opposite sign; the effect being more marked in the case of P —.

This admits of the following explanation:—With a plate opposite P (open circles), there are, just at the commencement of the discharge, practically no ions present between P and E. With a point opposite P (filled circles) there are definitely, at the instant of P's discharge, ions of one sign between P and E (viz. those supplied by N, which discharges before P), and these ions contribute their lines of force to the field already present.

Hence the potential of E would be higher in the latter case than in the former, whether P is positive or negative. The fact that the increase is greater for P negative is readily explained. It was found that the current, supplied by N, necessary to produce discharge from P, is greater for P− than for P+. This, together with the fact that the external ions in the former case are the slower moving positives, implies that the increase in the potential drop close to P, due to these ions, must be greater when P is negative.

Now the pull readings appeared to indicate that, in the case of P+, the field at the surface of the point was less when external ions were supplied than with no external ions. The potential drop in the distance of 2 mm. from P does not show this effect. The superposed potential drop due to the supplied positive ions may, of course, be more than sufficient to swamp the effect; but in any case it seems clear that without further information as regards the variation of potential throughout the 2 mm., we cannot, from the present values of this potential drop, obtain reliable evidence of the value of the field at the surface of P. The sparking effect mentioned above prevents the obtaining of this information.

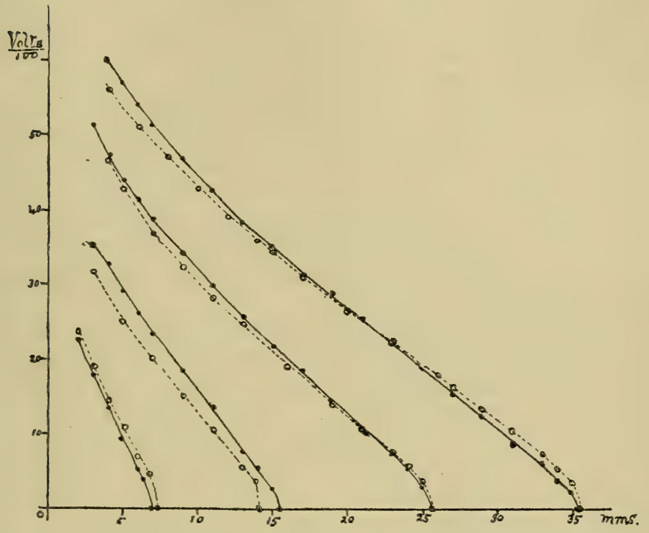
The most that can be said, therefore, is that the measurements of potential drop near the point, when external ions are supplied, are in agreement with the results of the pull measurements of the field at the surface of the point, in those cases in which the information obtained is complete.

Potential readings near the plate.—With the same apparatus the slope of potential along the central line between the electrodes, in the case of a point discharging on to a plate, was investigated. For this P was connected to the wimshurst and the plate was earthed through the galvanometer.

The potential slope was traced by means of E for different values of distance between the electrodes (x) and of current (C).

Curves III. show some of the results for different values of x (C=3·1 microamps.), the full curves representing positive discharge from P, and the broken ones negative. The intercept made by each curve on the horizontal axis gives the corresponding value of x (the plate being at zero potential). It appears that the potential slope is more or less uniform near the plate, except within about 1 mm. of the latter, when there is invariably a marked increase. Now Warburg (*Ann. der Phys.* iv. 2, p. 299) obtained some results by the same method, for the same values of x, and found a marked change in slope quite close to the plate, the potential drop there being, in some cases, as much as one fourth of the total fall of potential between point and plate. Furthermore, since the completion of the author's experiments on this part of the work, Hovda (Phys. Rev. Jan. 1912) has published a curve of potential gradient for the much greater distance of 50 cm., and this exhibits, near the plate, a drop which is only a very small fraction of the total drop between the electrodes.

Curves III.



The author's curves, for various shorter distances, agree in shape with that of Hovda for a great distance, and not with Warburg's earlier ones.

The following considerations present themselves:—

(i.) The existence of a true drop in potential near the plate, such as occurs at the electrodes in glow discharge at low pressure. This is unlikely, since the observed effect extends at least a millimetre from the plate, and there was no glow at the plate.

(ii.) The presence of free ions in the space between the electrodes. These should cause an increase in the potential gradient as the plate is approached, provided the divergence of the lines of force between point and plate is not too great. But such an effect would not be confined to the region within a millimetre or so of the plate. Moreover, the drop at the plate was found to occur for currents so small that the effect of the free ions must have been negligible.

(iii.) The well-known view that an exploring wire, in a region where one sign of ion predominates, takes up too high a potential, as pointed out by Sir J. J. Thomson.

It was at first thought that this error, if present, might be eliminated by a small leak on the electrometer. By comparing the effects of different leaks it was thought that a value of the leak might be found which would keep the exploring wire at the true potential of the air in its neighbourhood. This would be the case if, upon adding a small further leak, no further fall in potential resulted. No such value of the leak could be found ; in fact, for higher potentials the shape of the curve was entirely altered by a small leak and indicated that in this region the exploring wire was below the potential of its surroundings. For the final experiments, therefore, leak was carefully avoided.

Another attempt was made to test whether the potential of the exploring wire is always too high. E was replaced by a loop of fine platinum wire, which could be made red-hot by an electric current. Potentials of the loop, when hot and when cold respectively, were measured at any given position. If the potential of the cold loop is higher than it ought to be, there should be a decrease in the electrometer deflexion when the heating current is switched on. The readings obtained were found to be irregular, probably owing to the large fluctuations in the temperature of the loop caused by the electric wind. On the whole, however, no great change, and certainly no marked decrease, was produced in the potential readings by heating the wire. This appears to show that the explorer E was actually indicating the true potential of the air at its surface.

(iv.) Disturbance may be introduced by the presence of the sheath of the exploring wire. This explanation is supported by the fact that the drop near the plate is not quite sudden. In the early experiments a glass sheath was used, but in order to ensure that the effect was not due to conduction at the surface of the sheath, quartz was substituted for the glass. More consistent results were obtained, but the sudden drop was not eliminated.

Hovda (*loc. cit.*) suggested a second method for tracing the slope of potential between point and plate. This consisted in replacing any given equipotential surface by a metal surface, earthing the latter, and measuring the difference in the potential of the discharge point necessary to maintain the same current as before: this difference gives the original potential of the equipotential surface. From curves of discharge-potential plotted with current, previously obtained for different distances between point and plate, Hovda constructed potential gradient curves, on the assumption that each equipotential surface may, in this case, be replaced by a plane. (Table I., in the present paper, gives a rough indication of how near to the point this assumption holds good.) This method throws no light on the nature of the drop at the plate. At present, therefore, the cause of this drop must be left uncertain, though probably the evidence is somewhat in favour of a disturbance effect.

Whatever may be its cause, if the effect is constant throughout the region near the plate, the field at the plate may be obtained from the potential gradient curves, by subtracting the observed sudden potential drop from the other readings in this region. Although the assumption is an arbitrary one, values of the field (f), of at any rate the right order of magnitude, were obtained in this way and tabulated for use in future work on point discharge (Table I.).

Table I.

P positive.		P negative.	
x.	f.	x.	f.
(mm.)	(volts/cm.)	(mm.)	(volts/cm.)
7·0	4060		
15·5	2670	7·3	3670
25·5	1830	14·1	2410
35·4	1640	25·5	1690
47·5	1370	35·3	1480
69·0	1250	68·0	1000

It is seen that the field increases as the distance between the electrodes decreases; this is due to the fact that, the field at the point being constant, the spread of the lines of force, and of the current, decreases as the distance decreases, and that therefore the field at the centre of the plate is increased.

Curves were obtained for different currents also (for

$x=35{\cdot}5$ mm.) and the calculated fields, for + and — discharge from P, are shown in the following table:—

TABLE II.

C.	f_+.	f_-.
(microamps.)	(volts/cm.)	(volts/cm.)
0·4	670	710
0·8	930	890
1·6	1270	1120
2·3	1480	1300
3·1	1640	1500

Summary.

The potential drop in the immediate vicinity of a point discharging on to a plate is independent of (*a*) the distance between the electrodes, (*b*) the current between the electrodes. The potential drop required to start discharge is slightly greater at a negative point than at a positive point.

The effects on the potential drop of supplying to the point ions from an external source have been investigated.

These results are discussed in the light of previous determinations of the field at a discharging point obtained from measurements of the mechanical pull on its surface.

The potential gradient in the vicinity of the plate has also been measured over certain ranges of current and distance.

These experiments were carried out in the Physics Laboratories of the University of Bristol.

I wish to acknowledge my indebtedness to Dr. Tyndall for the constant advice and suggestion he has offered, and to Mr. J. D. Fry for help in the construction of the apparatus.

LVII. *Photographic Registration of α Particles.* *By* Dr. H. GEIGER *and* Prof. E. RUTHERFORD, *F.R.S.*, *University of Manchester* *.

IN a previous paper † the authors have described an electrical method of counting the α particles from radioactive substances. For this purpose, the α particles passed through a small opening into a cylindrical vessel which contained air or another gas at a reduced pressure. The cylinder was provided with a central electrode which was connected with an electrometer, and the outer cylinder was charged to a negative potential nearly sufficient to cause the passage of a spark. Under such conditions, the small ionization produced by the α particle is magnified several thousand times by collision, and the entrance of an α particle into the testing vessel is signalized by a ballistic throw of the electrometer-needle. In order to determine the number of α particles emitted per second by one gram of radium, a source of small diameter coated with radium C was placed at some distance from the opening in an exhausted tube, so that a definite fraction of the α particles passed through the mica-covered opening of the detecting vessel.

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* Communicated by the Authors.

† Rutherford & Geiger, Proc. Roy. Soc. A. lxxxi. p. 141 (1908).

Since the electrometer responds only slowly to the rise of potential caused by the entrance of an α particle, it was not possible to count with accuracy more than about 10 α particles per minute. Since our original experiments, several types of string electrometers have been devised. The moving part consists of a thin silvered quartz fibre placed between two charged parallel plates. The fibre follows rapidly any change of potential applied. In 1910 we used a string electrometer, devised by Laby and constructed by the Cambridge Scientific Co., for the purpose of counting α particles. The instrument was found to have sufficient sensibility, and the movement of the fibre produced by the entrance of each α particle into the detecting vessel could be simply recorded on a moving photographic film.

A number of investigations have been made from time to time in order to find the best conditions for obtaining a clear record of the individual α particles even when they enter the detecting vessel in very quick succession. The conditions for accurate counting depend on the following :—

(1) The absence of electric disturbances in the detecting vessel when no α particles enter.
(2) The equality of throws for each α particle.
(3) The elimination of the effect of scattering of the α particles in the mica window and the gas in the detecting vessel.

For accurate work, it is essential that the fibre after displacement should return rapidly to its equilibrium position. To achieve this purpose, the fibre was connected through a comparatively low resistance to earth. Suitable resistances can be simply made by using capillary tubings filled with a mixture of xylol and alcohol *. The back leak so provided

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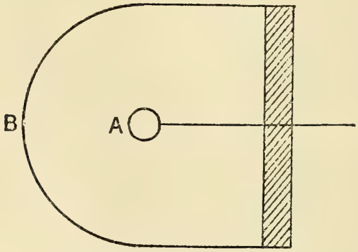
* Campbell, Phil. Mag. xxiii. p. 668 (1912).

is ordinarily very much greater than can be used in counting with the quadrant electrometer. This large back leak has the great advantage of cutting out the great majority of slow electrical disturbances, for only rapid changes of potential make their effects visible.

The type of cylindrical vessel used in our original investigations did not fulfil condition (2) on account of scattering of the α particles by the mica-covered opening through which they entered. On account of this scattering, the α particles have different lengths of path in the gas, and produce unequal throws. The differences in the throws become less marked the smaller the length of the tube compared with its diameter. To overcome this difficulty, a detecting vessel of the type shown in fig. 1 was constructed.

Fig. 1.

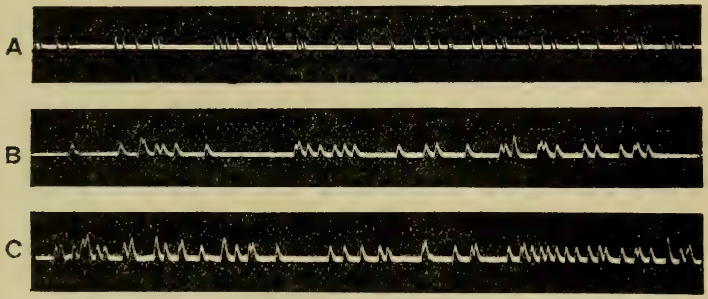


It consisted of a metallic hemisphere, near the centre of which was a spherical electrode A supported by a metal rod. The α particles entered in the hemisphere through the opening B which was covered with a thin sheet of mica. Helium at suitable pressure was introduced into the apparatus. With this arrangement, it was found that the throws were remarkably uniform, so that it was easy to recognize by the length of the throw when two or even three α particles entered the vessel in rapid succession.

In these experiments we have used helium at a pressure of about one-third of an atmosphere as the gas in the detecting vessel. The use of helium has many advantages. In the first place, the potential difference required is much lower than with air or carbon dioxide at the same pressure. This potential was found to increase very much when small impurities were present with the helium. As is well known, however, the helium can easily be purified by passing it over charcoal cooled by liquid air. This method of purification of helium was used in all the experiments. Using helium in the detecting vessel, the necessary magnification could easily be obtained, and the magnitudes of the throws remained unchanged for hours at a time. In addition, hardly any natural disturbances were observed when the α particles did not enter. In the particular apparatus employed, the α particles travelled a distance of 3 cm. in the helium. With a pressure of 20 cm. the stopping power of the α particles in the gas corresponded to only 2 millimetres of air at atmospheric pressure. At a pressure of 20 cm. each α particle produced a large electrical effect ; but even when the pressure was reduced to 5 millimetres, the entrance of each α particle could be easily detected by the movement of the fibre of the electrometer. At this latter pressure, the stopping power of the α particle corresponded to only ·06 of a millimetre of air. In these circumstances, about 400 volts only were required to give the necessary magnification. These results bring out the enormous increase in the number of ions produced by collision under these conditions.

It is not possible to count with certainty by eye observations more than about 50 throws of the fibre per minute. The fibre moves so rapidly that it is difficult to recognize when two or more α particles enter the detecting vessel at very short intervals. It is far more certain to use a photographic method for recording the rapid movements of the fibre. For this purpose, we have found the registration apparatus constructed by Professor Edelmann very serviceable. The speed of the film could be regulated over a wide range according to the number of α particles to be registered per minute. The types of record obtained for the different rates of entrance of the α particles are illustrated in fig. 2.

Fig. 2.



The line A shows the part of the record obtained when the film moved at a rate of 13 cm. per minute, and for an average of 50 α particles per minute. The length shown on the photograph corresponds to an interval of about 1 minute.

The line B corresponds to a movement of the film of 180 cm. per second and for about 600 α particles per minute. The line C corresponds to an average of 900 α particles per minute.

It is seen that a clear record is obtained of the movements of the fibre even when on an average 15 α particles enter per second. With eye observations, the movements of the fibre appeared blurred and confused, but the photograph brings out clearly each individual movement. With a little experience, it is not difficult to count the number of α particles that have entered the detecting vessel in a given interval even at the rate of 1000 per minute.

The experiments described in this paper have been made with a view to determining the best conditions for measuring with accuracy the number of α particles expelled from radioactive substances, and in particular, for re-determining the number of α particles expelled per second from one gram of radium. A lengthy series of observations will be required before the value of this important constant can be definitely settled.

Recoil atoms.—It is well known from the experiments of Hahn [*] and of Russ and Makower [†], that the emission of α particles from radioactive substances is accompanied by a vigorous recoil of the residual atoms. The recoiling atom is able to penetrate about 1/10 of a millimetre of air and of about 4/10 of a millimetre of hydrogen at atmospheric pressure, before being stopped. Wertenstein [‡] has shown that these recoil atoms produce a strong ionization in the gas they traverse. This has been observed by determining the ionization due to recoil atoms and α particles at low pressures. Under these conditions, the recoil atom appears to cause several times the ionization due to an α particle over the same range.

We have seen above that it is not difficult to detect the electrical effect of a single α particle when it traverses a gas at such a low pressure that its range is only reduced by 1/20 of a millimetre. This is less than the range of the recoil atom, and it thus seems probable that the electric method could be employed to detect a single recoil atom. Some experiments were made as follows :—the mica window over the opening of the detecting vessel was removed and the radiation from a plate coated with the active deposit of actinium was allowed to enter the detecting vessel, which contained helium at a pressure of about 8 millimetres. Such an active plate causes a vigorous recoil of the atoms of actinium D. Some throws were observed large compared with those of the α particle ; but the interpretation of the experiments is complicated by the natural disturbances due to the uncovered opening and to the strong ionization produced by the radiating source outside the opening. Further experiments are in progress to test whether this method can be employed to count the recoil atoms with certainty.

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[*] Hahn, *Verh. d. D. phys. Ges.* xi. p. 55 (1909).

[†] Russ & Makower, Proc. Roy. Soc. A. lxxxii. p. 205 (1909).

[‡] Wertenstein, *C. R.* clii. p. 1657 (1911).

University of Manchester,
August 16, 1912.

LVIII. *On the Influence of the Physical Conditions of a Substance on its Absorption of Light.* *By* G. H. LIVENS, *B.A., Fellow of Jesus College, Cambridge* *.

IN a recent communication to this Journal I have given a discussion of the effect of the density of a gas on its line spectrum. The results there obtained have, however, a wider application than appeared at first sight. An explanation of several other experimental facts concerning the effect of the physical circumstances of a substance on its absorption of light also appear to be contained in the theory. An interesting account of the phenomena under discussion is given by Prof. Wood in his book on 'Physical Optics.'

A few of the results here obtained have already been deduced by Dr. Havelock †, and the reader is referred to that author's papers for a more complete discussion. Dr. Havelock's results however, are, owing to their generality, exhibited in rather a complicated form, and it seems as well to present them in the much simpler form in which they are deducible from the present theory.

1. *The influence of the nature of the solvent upon the position of the absorption bands of the dissolved substance.*—Wood gives a short account of Kundt's work on this subject, and summarizes the results in the following statement of Kundt's law:—If one transparent medium has a higher refractive index than another, the absorption bands of a dissolved substance lie nearer the red end of the spectrum when it is dissolved in the former than when it is dissolved in the latter.

I shall now adopt the notation of my previous paper and quote the results there deduced. The equation of motion of the typical electron of mass m and charge e was taken in the form

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* Communicated by the Author.

† Proc. R. S. 1910, 1911.

$$m\ddot{x}+h\dot{x}+kx=e(\mathrm{E}_x+a\mathrm{P}_x),$$

where, E_x is the x-component of the electric force and P_x that of the polarization intensity. It was then found in the usual way that the absorption coefficient for light of a frequency $(n_0+\xi)$ was

$$\mu k=\frac{1}{2}\frac{\rho_1 n_0 n_1'}{[(1-a\mathrm{A})2n_0\xi+a\rho_1]^2+(1-a\mathrm{A})^2 n_0^2 n_1'^2},$$

where, if N_1 is the number of electrons with the natural free period $n=n_0$,

$$\rho_1=\frac{\mathrm{N}_1 e^2}{m},\quad n_1'=\frac{h_1}{m},$$

and

$$\mathrm{A}=\Sigma\frac{e^2}{k-mn_0^2},$$

this sum being taken over all the electrons per unit volume which have not the natural free period $n=n_0$.

From this we deduce at once that the maximum absorption is of amount

$$\mu k=\frac{1}{2}\frac{\rho_1}{n_0 n_1'(1-a\mathrm{A})^2}, \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

and occurs not in the position $\xi=0$ $(n=n_0)$ but displaced towards the red end of the spectrum through a distance given by

$$\xi=\frac{a\rho_1}{2(1-a\mathrm{A})n_0}.$$

Now consider for simplicity the case when the spectrum of the dissolved substance consists only of a single line corresponding to the frequency $n=n_0$, and that this line does not occur in the absorption spectrum. The value of A then arises entirely from the electrons in the solvent. Moreover, if μ is the index of refraction of the solvent for the particular light of frequency $n=n_0$, then

$$\mu^2=1+\frac{\mathrm{A}}{1-a\mathrm{A}}$$

$$=\left(1-\frac{1}{a}\right)+\frac{1}{a}\cdot\frac{1}{1-a\mathrm{A}}.$$

Thus an increase in μ arises mainly from an increase in the term $1/(1-a\mathrm{A})$. That is, an increase in μ corresponds to an increase in the displacement of the absorption lines towards the region of longer wave-length. This is Kundt's result.

Also according to Wood there appears to be evidence that the position of an absorption band depends on the concentration of the solution. This, of course, is exactly analogous to the case discussed in the previous paper. An increase in the density of the absorbing electrons displaces the line proportionately to the red end of the spectrum.

2. *Absorption in a gas.*—It is generally assumed that the absorption produced by a given quantity of gas is independent of its density. The important discovery was, however, made by Ångström that the compression of a gas increased the intensity of its absorption, the mass of gas traversed remaining the same. The general results of this and much subsequent work of a similar kind are summarized by Wood in the four following statements :—

1. Beer's law does not in general hold for gases.
2. If to a gas at a definite volume we add a foreign gas which does not act on it chemically, its absorption is increased.
3. The absorption of a gas mixture is greater than the sum of the absorptions of its separate constituents each one taken at its partial pressure.
4. The absorption of a gas mixture is, on the contrary, equal to the sum of the absorptions of its constituent parts if each part is taken at a pressure equal to the total pressure.

Now equation (i.) above shows that the maximum absorption coefficient is

$$\mu k = \frac{\rho_1}{2n_0 n_1{}'} \cdot \frac{1}{(1-a\mathrm{A})^2}$$

and results (1) and (2) above are direct deductions from this formula. The simple statement contained in (4) does not appear, however, to be exact; although it is probably approximately true for the case of gases.

It is important to notice that the results of this and the last paragraph are simply two aspects of the one general problem. In the case of liquids the point investigated appears to have been the displacement of the absorption lines, their intensities being left out of consideration. In the case of gases it appears to have been the alteration in the intensity which first attracted notice. The two phenomena should, however, be present in both experiments, and the theory is equally valid for the two cases.

3. *On the broadening of the lines of a spectrum with increasing density.*

We shall now turn to the last type of effect which is generally concerned with the alteration in the appearance of the lines or bands in a spectrum produced by changing the physical conditions. It is to be noticed that the theory here given will apply equally well to both emission and absorption spectra.

The theory in its present form does not, however, offer any explanation of a phenomenon of this kind; but an obvious and fairly plausible extension makes most of the experimental results so obvious that, on these grounds alone, it might be claimed as the effectively correct explanation. The extension is arrived at by a reconsideration of the constant a which occurs in our formulæ. It was introduced as the coefficient of the polarization in the expression for the force on unit charge in a small cavity in the polarized medium. This expression represents simply the local part of the total forcive acting on a charge placed there, and arises entirely from the molecules in the immediate neighbourhood. Such a quantity, of course, is quite indeterminate in any real case, but an ideal estimate gives $a=1/3$. In an actual case the constant would approximate more or less accurately to this limiting value. Now in discussing spectrum lines in the above manner, we have to deal separately with the oscillations of each individual electron, and a value of this constant a has to be used for each one. Now it seems most probable that the constant a is not a constant for each individual electron but varies from one electron to another. It seems in fact that it would be better to take a range of more or less probable values grouped about the ideal value $a=1/3$. Moreover, the actual facts seem to indicate that the extent of the range should decrease as the condition of the substance approaches the limiting condition, *i. e.* the ideal limit of gas theory (practically when the density $\delta=0$). Moreover, the range cannot extend beyond the value $a=0$ on the one side; but except for the conditions implied in the analytical approximations, there seems to be no reason to exclude indefinite extension on the other side. Without attaching any special significance to the form of the functions given, I shall, for the sake of argument, assume that the range of most probable (not necessarily equally probable) values is bounded by the values

$$a=\frac{1}{3}\cdot\frac{1}{1+c_1\delta}, \qquad a=\tfrac{1}{3}(1+c_2\delta),$$

where c_1 and c_2 are constants of each line and δ the density.

Under these assumptions the single line in the "ideal" spectrum of the substance corresponding to a frequency $n=n_0$ would be broadened out into a band whose brightest part would lie between the two positions at distances to the red side of the position $n=n_0$,

$$\xi_1 = \frac{\rho_1}{2n_0} \cdot \frac{1}{1+(1+c_1\delta)(1+c_2\delta)},$$

$$\xi_2 = \frac{\rho_1}{2n_0} \cdot \frac{(1+c_2\delta)(1+c_1\delta)}{1+(1+c_1\delta)(1+c_2\delta)}.$$

If we assumed that each value of a between the above limits were equally probable for any one electron, the portion of the band between ξ_1 and ξ_2 would be uniformly bright. Inequalities in the probability of the occurrence of the various values of a, which it seems more reasonable to assume, would account for differences in the intensity of the various parts of the band, the brighter parts corresponding to the more probable values of a. A simple explanation of the constitution of channelled spectra seems to be here involved ; but this point is reserved for future consideration.

The value of ρ_1 in the above formulæ is also proportional to the density of the substance, and so we can write

$$\xi_1 = \xi_0 \frac{\delta}{1+(1+c_1\delta)(1+c_2\delta)},$$

$$\xi_2 = \xi_0 \frac{\delta(1+c_1\delta)(1+c_2\delta)}{1+(1+c_1\delta)(1+c_2\delta)};$$

and therefore the breadth of the band is

$$\xi_2 - \xi_1 = \xi_0\delta \frac{(1+c_1\delta)(1+c_2\delta)-1}{(1+c_1\delta)(1+c_2\delta)+1}.$$

This result enables us to deduce at least a qualitative explanation of the effect of an increase in density on the lines of the spectrum. The broadening out of the line is always much faster towards the side of longer wave-length. In fact the broadening towards the violet side, although practically symmetrical with that on the other side when the density is small, soon becomes very slow. This explains the unsymmetrical broadening of most of the lines of ordinary spectra. An explanation of some of the remarkable phenomena discovered by Wood particularly in the mercury line 2536 is also involved.

The extension of the above ideas to include the action of a foreign chemically inactive gas is of course obvious. The theoretical conclusions derived agree with the experimental results given by Wood.

This theory also provides for the broadening of the lines in Humphrey's experiments on the "pressure shift." There is, however, a still more obvious reason for taking a range of values of the constant a as above. The density of the gas varies considerably from the cooler parts in the surrounding air to the very hot portions in the centre of the arc.

It thus appears that by taking advantage of the latitude allowed by the theoretical uncertainty in the value of the constant a, we can explain a large number of the complications present in ordinary spectra. We have merely to avoid mutually inconsistent hypotheses in explaining the various types of the phenomena. Any consistent and reasonable set of properties for the constant a would appear to provide a theoretically effective explanation of the phenomena under discussion. We might regard the experimental results as providing the necessary laws for the variation of the constant a with the physical conditions of the material. It is, however, important to notice that the more extensive list of physical properties would involve only the mean value of the constant a taken for all the electrons of the substance. Such values are deducible from known properties of the substance in bulk. Spectrum analysis alone can separate out the possibly different values of a with which we are concerned when discussing the individual electrons.

Dr. Havelock has given a discussion of the dependence of the mean value of the constant a on the physical conditions of the substance.

The theory here given is not, however, complete. It appears to fail in one very important respect. Although in the majority of cases the actual facts are as stated, yet there are some important exceptions. For instance, the displacement of certain absorption and emission lines in the spectra of not uncommon substances is *not* towards the red end of the spectrum, but towards the violet end. The associated phenomena of asymmetrical broadening also frequently takes place in this direction. The theory here developed appears, at present, quite unable to admit of an explanation of these divergences from what appears, after all, to be the general rule which it does so well explain. Further investigation may, however, confirm the results already deduced: and we must then look for the loophole which will enable us to extend the theory to the above anomalies.

LIX. *Note on the Elasticity of Liquid Films and the Foaming of Solutions.* *By* S. A. SHORTER, *B.Sc., Assistant Lecturer in Physics in the University of Leeds* *.

IN the July number of the Philosophical Magazine, Prof. Pollock raises some interesting questions with regard to the foaming of solutions. I have been engaged for some time in theoretical and experimental investigations relating to this subject, and perhaps a short preliminary account of my theory of the elasticity of liquid films will throw some light on these questions.

According to Gibbs's theory of capillarity, a solute, the further addition of which to the solution lowers the surface tension, will be more concentrated in the surface layers than in the body of the solution. Gibbs obtains an expression for the "surface excess" which involves the chemical potentials of the components of the solution. I have extended Gibbs's theory and obtained expressions for the practical calculation of the surface excess, applicable to solutions of any degree of concentration. This general theory is rather complicated. The present discussion is limited to the case of an ideal dilute solution. This limitation, while it simplifies very considerably the mathematical treatment, does not deprive the discussion of any of its physical essentials. In the case of an ideal dilute solution, my theory leads to Milner's † well-known expression

$$\Gamma=-\frac{c}{\mathrm{R}\theta}\frac{\partial\tau}{\partial c},$$

where Γ is the surface excess (per unit area of surface), τ the surface tension, θ the temperature, R the gas constant, and c the concentration (in mass of solute per unit volume of solution).

The extension of a film of a pure liquid causes no increase in the surface tension. Hence such a film can have only a brief existence. Thus if different parts of the film are at different levels, gravity will lead to an indefinite thinning of the upper parts, and hence to the rupture of the film. The case of a film of a solution, in which the solute has a marked lowering effect on the surface tension, is quite different. If such a film be extended, equilibrium between the surface layers and the interior of the film is disturbed, and the tension is increased. While this equilibrium is being re-established the tension will decrease, but not to its original value, because the amount of solute drawn from the interior of the film will be large enough to cause a diminution of concentration sufficient to increase appreciably the surface tension.

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* Communicated by the Author.

† Phil. Mag. vol. xiii. p. 96, Jan. 1907.

The magnitude of this elastic effect is easily calculated. Suppose that a film of thickness t is held in a rectangular framework of length h and breadth b, and suppose that one of the sides (which is supposed to be movable) is moved so that the length of the film is increased to $h+\Delta h$. This causes an increase $2b\Delta h$ in the area of the film, and if we neglect the effect of the variation of the surface excess with the concentration * the amount of solute drawn from the interior of the film, to form the new surface excess, is $2\Gamma b\Delta h$. The consequent change of concentration is given by †

$$\Delta c = -\frac{2\Gamma\Delta h}{ht},$$

and the change of surface tension by

$$\Delta\tau = -\frac{2\Gamma\frac{\partial\tau}{\partial c}}{ht}\Delta h.$$

Let us consider the stretching effect produced by gravity when the film is placed with its length vertical, and the movable side (which is supposed to be weighted to support the initial tension of the film) downward. To support the weight of the film, the highest parts of the film must be extended so that the tension is increased by an amount $\frac{1}{2}\rho ght$ (where ρ is the density of the solution). The tension in the lowest parts of the film will be unaltered. Hence we may regard the stretching produced as equal to that which would be produced by an increase of half the weight of the film in the force acting on the movable side, *i. e.* we must write

$$\Delta\tau = \tfrac{1}{4}\rho ght$$

in the preceding equation. We thus get the following expression for the extension of the film

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* This amounts to neglecting $\partial\Gamma c$ in comparison with t, which is allowable, except in the case of extremely dilute solutions.

† In the more general theory, applicable to solutions of any degree of concentration, it is necessary to take into account the amount of solvent expelled from the surface layers.

$$\Delta h = -\frac{\rho g h^2 t^2}{8\Gamma \frac{\partial \tau}{\partial c}}.$$

As an example of the practical application of this formula, we will take the case of an aqueous solution of valeric acid of concentration ·0048 grm. per c.c. From Traube's * surface-tension measurements we obtain the value

$$-\frac{\partial \tau}{\partial c} = 2200 \frac{\text{dyne cm.}^2}{\text{grm.}}.$$

Milner's formula gives

$$\Gamma = 4{\cdot}4 \times 10^{-8} \frac{\text{grm.}}{\text{cm.}^2},$$

so that

$$-\Gamma \frac{\partial \tau}{\partial c} = 9{\cdot}7 \times 10^{-5} \text{ dyne.}$$

Hence if h and t are expressed in cm. we have

$$\Delta h = h^2 t^2 \times 1{\cdot}3 \times 10^6 \text{ cm.}$$

If we assume the comparatively large values $h = 1$ cm. and $t = 10^{-4}$ cm. we have

$$\Delta h = 1{\cdot}3 \times 10^{-2} \text{ cm.}$$

Hence a film 1 cm. high and 1000 $\mu\mu$ thick would stretch only about one-eightieth of its height under its own weight.

We see that the elasticity of a film of a solution is determined by the magnitude of the product of the surface excess and the rate of decrease of the surface tension with increasing concentration. This quantity may therefore be regarded as a measure of the foaming power of a solution. If the quantity were evaluated for a number of solutions, we should expect those solutions, for which the value was relatively high, to possess the property of forming a durable foam. At present I am investigating the relation between this quantity (or the corresponding quantity in the more general theory) and the foaming power of solutions.

In the case of solutions of the type we are considering, the value of $-\Gamma \partial \tau / \partial c$ increases at first with increasing concentration, and then diminishes as the concentration is further increased. This is in agreement with the experimental fact

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* *Lieb. Ann.* vol. cclxv. p. 30 (1891).

that increase of concentration beyond a certain point is detrimental to the foaming power.

It cannot be claimed that this simple statical theory gives a complete explanation of the essentially dynamical process of foaming. Nevertheless a comparison between theory and experiment, even if it simply demonstrates the insufficiency of the theory, will yield valuable information as to the nature of the process*.

The University, Leeds,
July 11, 1912.

LX. *On the Supply of Radium Emanation from the Soil to the Atmosphere. By* Louis B. Smyth, *B.A., Assistant to the Professor of Geology in the University of Dublin* †.

[Plate XIV.]

THE present investigation was undertaken as an extension of similar work carried out by Professor Joly and myself last summer ‡.

In the course of that work the amounts of radium emanation contained in the gases diffused through the soil were estimated for various depths, and from day to day; and observations were made on the amount escaping from the surface of the soil. The short series of observations thus obtained, besides showing that the amounts of emanation found to be escaping from the soil are quite adequate to account for the amounts found in the atmosphere, appeared also to show that "progressive variations in the amount of emanation exhaled from the soil are attended by progressive changes in the other direction in the amount of emanation accumulating beneath the surface," and that "fine weather tends to diminish, and wet weather to increase the richness of the ground gases."

It was thought desirable to obtain a longer and more regular series of simultaneous experiments on the amounts of emanation being exhaled and accumulating respectively. Consequently two series of experiments were started on August 16th last year, and carried on simultaneously every two days until March 5th this year. One series dealt with the emanation content of ground-gas drawn from 50 cm. below the surface, the other with the escape of emanation from the surface at an adjacent spot.

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* Experiment seems to show that of two solutions for which the quantity $-\Gamma\partial\tau/\partial c$ has the same value, the more dilute has the greater foaming power. This indicates that the slowness of establishment of equilibrium between the surface layers and the body of the film is a factor of importance in the case of very dilute solutions.

† Communicated by the Author.

‡ Proc. Royal Dublin Society, xiii. p. 148, Aug. 1911.

The observations were made on a lawn beside the School of Engineering, Trinity College, Dublin. The soil is calcareous, well-drained, and several metres deep.

Method.

1. *Soil Gas.*—The estimation of the amount of emanation contained in the gases occupying the interstices of the soil is carried out as follows. An iron pipe, of 15 mm. bore, is closed and pointed at the lower end. Holes are drilled in its walls near this end. These slope downwards and inwards to prevent clogging when the tube is being driven into the ground. To reduce the capacity of the pipe as far as possible, a loosely fitting, closed brass tube is inserted. The upper end of the iron pipe is fitted with a glass leading tube, which is usually kept closed. The pipe was in these experiments driven into the soil so that the holes near the end were 50 cm. from the surface.

A litre boiling-flask was used to collect the soil gas. It is exhausted of air and attached to the leading tube. The connexions being opened, gas flows from the soil spaces into the flask. The flow is observed by causing the gas to bubble through a little water at the bottom of the flask. The flask, when full, is allowed to stand at least 10 minutes to allow any thorium emanation present to decay to a negligible amount. The flask is now attached to an exhausted electroscope (capacity 600 c.c.) and the gas allowed to flow into the latter, water being allowed to flow into the flask to take the place of the gas. The rate of discharge of the electroscope is now read for a short time, and again in about three hours. These rates, less the normal rate of discharge, ascertained just before the experiment, allow one to estimate the amount of emanation present, the electroscope having been calibrated by the emanation from a known amount of radium. The results are reduced to amounts of emanation per litre, and are expressed in curies $\times 10^{-12}$.

2. *Exhalation.*—To estimate the amounts of radium emanation given off from the surface of the soil, the following method was used. The collecting vessel is of tin-plate, cylindrical, 25 cm. in diameter and 8 cm. deep. One end is closed but for a central opening 3 cm. in diameter. The other is open and its edge is pressed into the ground. Inside this vessel is a circular plate of tin 24 cm. diameter, resting on feet about 3 cm. long. This plate has a central opening

1 cm. in diameter from which a vertical tube rises through the opening in the top of the tin vessel. From this tube a line of lead and rubber pipes run to a suction-pump in the laboratory, a distance of about 45 feet. Immediately before each experiment the tin vessel was placed in position, usually not on the same spot it occupied during the next preceding experiment. When suction is applied, air enters by the aperture in the tin vessel, flows over the margin of the tin disk, and, after sweeping over the surface of the ground, and presumably carrying away any emanation given off therefrom, it enters the system of pipes. On arriving in the laboratory it is made to traverse a quartz tube of 1·5 cm. bore, containing coarsely powdered coconut charcoal which absorbs the emanation. The rate of suction was usually about 20 litres per hour; but variations in this were not found to have any noticeable effect, as probably a much slower current would be sufficient to carry away all the emanation exhaled. When the suction has continued for an hour, the quartz tube is attached to a rubber bag, and heated in a gas-furnace for about half an hour. The contents of the bag and tube are then transferred to an electroscope which is observed as before.

The results are reduced to amounts of emanation escaping from 1 sq. m. per hour, and are, as before, expressed in curies $\times 10^{-12}$.

The error due to the amount of emanation in the atmosphere at the time of the experiment has been neglected.

Results.

The results of the two series of experiments have been plotted together (Pl. XIV.), the exhalation results having been divided by 100 in order to have them close to the others. The dates are marked on the abscissa line. The ordinates are amounts of radium emanation in curies $\times 10^{-12}$. The full line represents exhalation, the broken line ground-gas. Along the top of the diagram the weather is indicated. In the weather indications S. stands for stormy, F. for frost.

As might be expected, the results are very irregular. The conditions influencing the escape of emanation from the soil spaces to the atmosphere are very complex, and the various factors interfere with one another. The exhalation, being less capable of exact determination under natural conditions, besides being probably more liable to rapid variations, will in general yield less reliable results than the ground-gas. The figures arrived at, too, only represent the state of things during one hour in forty-eight.

Experiments were attempted with a view of getting some idea of the variation of emanation outflow from hour to hour. The current of air from the collector was led directly through an electroscope, and the rate of discharge observed continuously. The length of tube (45 feet) connecting the collector with the electroscope, and the slow rate of air-flow necessary in order that the draught might not disturb the gold-leaf, ensured the decay of thorium emanation before reaching the electroscope.

Before attaching the end of the suction-tube to the collector, the former was supported about 5 ft. above the surface of the soil, so that a current of atmospheric air flowed through the electroscope for a few hours. The rate of discharge was observed during this time. The tube was then attached to the collector, and the rate of discharge read again during some hours.

It was found that, in most cases, the emanation was too dilute to produce any appreciable effect on the rate of discharge. The following three experiments, however, gave results :—

	Rate of discharge in scale-divisions per hour.				
	Before attaching collector.		After attaching collector.		
1912.	Length of time observed.	Rate.	1st hour.	2nd hour.	3rd hour.
12 Jan. ...	1½ hours	5·3	12·4	8·7	—
14 Jan. ...	50 mins.	6·1	9·4	10·0	8·4
2 May ...	2 hours	5·0	6·6	7·5	8·6

These meagre results at least show that there may be considerable differences from hour to hour in the amount of emanation escaping from the soil, and that too much significance must not be attached to the details of the exhalation curve.

We may, I think, conclude from a study of the curves that there is no seasonal factor involved.

The condition which seems to have the most distinct effect is wind strength. A strong wind is very frequently accompanied by an increase in the amount of emanation escaping and a diminution in the amount registered below the surface. This phenomenon may be traced on the following dates (see curves) : Aug. 24–26, Sept. 1, 23, Oct. 21, Nov. 6, 14, 30, Dec. 8, 18, 24. (In the case of Aug. 24–26 the maximum and minimum respectively may quite possibly have occurred together on Aug. 25.) Maxima in the exhalation curve also occur on Nov. 16 and Mar. 3 accompanied by wind. The only remarkable exceptions occur on Sept. 15 and Feb. 28, and in both these cases there is a considerable drop in the emanation content of the soil-gas in the next experiment. It will be noticed that for the month of December the ground-gas curve exhibits a remarkable series of oscillations. These seem to be due to the fact that between the 4th and 24th of that month there were five severe gales, besides several lesser storms.

It is probable that when a gust of wind moves over the surface of the soil it exerts suction on the soil capillaries. The soil-gas, rich in radium emanation, is sucked out, and, when suction ceases, is replaced by dilute gas. Thus escape of emanation is caused by wind. The dilution of the upper parts of the soil-gas as regards emanation steepens the emanation concentration gradient, and thus increases the rate of upward diffusion. This would account for the depletion at 50 cm. so often accompanying storm in the experiments.

It is interesting to notice that the soil-gas curve attains its highest value on 31st January—the first experiment performed with the ground frozen. This may, perhaps, be attributed to the fact that the frozen surface prevented the escape of emanation. The high figure obtained on the same day for the escape of emanation may probably be accounted for by the fact that the collecting tin had to be pressed into the frozen soil, thus breaking the hard crust. We should expect a great outflow at this point, owing to the increased amount accumulated just below the surface.

In the following experiment the ground was harder, and the collector was driven in with a hammer. Perhaps it did not go deep enough to pierce the frozen crust, then presumably thicker. The exhalation result is the. lowest recorded. On the 4th Feb. the collector was only pressed into the snow until it touched the frozen ground.

A number of high readings occur from Dec. 30th to Jan. 9th on the soil-gas curve. These seem to be due to the fine, calm weather, accompanied by a heavy water-logged soil, which would hinder the escape of emanation.

As noticed in the previous experiments, rain tends to choke the soil capillaries and cause an accumulation of emanation below the surface. To observe this, we must examine the ground-gas curve at points where the wind factor does not interfere. For instance, on the following dates, wet weather, unaccompanied by wind, is followed by a rise in the amounts of emanation at 50 cm.:—Sept. 4, 12, 23–29, Oct. 3, 14, 23, Nov. 8, Dec. 26, Jan. 5, 17–21, 25, Feb. 8, 18. The only marked exception occurs on Oct. 27–29.

An examination of the barometric chart for the period covered by the experiments does not reveal any influence of atmospheric pressure on the results, except in so far as its fluctuations are accompanied by storm, rain, &c.

The average amounts of emanation found in these experiments should be of interest. They are as follows:—

Ground-gas (102 experiments) 163×10^{-12} curie per litre.

Exhalation (98 experiments) 2673×10^{-12} curie per sq.m. per hour.

In the course of the previous experiments referred to *, 38 observations on *ground-gas* were made, at the same place as the present ones, but at depths varying from 20 to 150 cm. The average of these was 180×10^{-12} curie per litre, which agrees fairly well with that given above.

The previous observations on *exhalation* were not made at the same spot. Ten of them were made about 30 ft. from the present ones, and 3 or 4 ft. from the wall of the laboratory, and twelve were made at a spot three miles away. These two sets gave averages of 839×10^{-12} and 4087×10^{-12} respectively.

Geological Laboratory,
Trinity College, Dublin,
July 1, 1912.

LXI. *A Comparison of the Coefficients of Diffusion of Thorium and Actinium Emanations, with a Note on their Periods of Transformation.* *By* MAY SYBIL LESLIE, *M.Sc.*†

THE values hitherto found for the diffusion coefficients of radium and thorium emanations differ considerably from one another. They are in general, however, except in the case of Perkins's experiments with radium emanation ‡, higher than would be expected from the probable molecular weights calculated on the basis of the disintegration theory, and practically confirmed by the values of the effusion coefficients found by Debierne[*] for radium emanation and by the author[†] for thorium emanation. No other data than the diffusion coefficient of the emanation are available for determining the molecular weights in the actinium series, and the results obtained in this direction suffer from the same uncertainty as in the case of the other emanations. For example, Debierne[‡] and Bruhat[§] both obtained ·112 as the diffusion coefficient in air at 76 cm. pressure and 15° C., whereas Russ[‖] obtained ·123. One would expect, however, to find the same disturbing cause, whatever it may be, operating in the diffusion experiments for all the radioactive gases. Therefore a comparison of the rates of diffusion of thorium and actinium emanations under strictly identical conditions should give the ratio of their molecular weights. If the value for thorium emanation is taken as 220, that for actinium emanation may then be calculated.

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* *Loc. cit.*

† Communicated by Prof. E. Rutherford, F.R.S.

‡ P. B. Perkins, Amer. Journ. of Sci., June 1908 xxv. p. 461.

Such a comparison was the object of the present investigation. Unfortunately, through the discovery of an unexpected source of error, no very definite conclusions could be drawn from the results, but as these throw some light on the cause of the discrepancies between the observed values for the diffusion coefficients, it will be useful to record them.

Experimental Arrangements.—The diffusion vessel was a glass cylinder of length 50 cm. and internal diameter 5 cm. It was closed at the top by a hollow ground-glass stopper to which was sealed, for communication with the exterior, a tube with two branches each provided with a tap. The bottom of the vessel was covered by a tray over which the substance providing the emanation was uniformly spread. The vessel was surrounded by a water-jacket, which kept it at a temperature sufficiently constant for the requirements of the experiment.

Preliminary Experiments with Thorium Emanation.—Thorium hydroxide dried at a gentle heat was used as the emanating source, and the distribution of emanation was at first measured by the active deposit on a metal plate down the centre of the tube. To both sides of the plate, across the end near to the substance, strips of tinfoil of equal width, about 4 mm., were attached. The exposures were from 15 to 20 hours, and no electric field was applied. Four or five hours after the removal of the plate, when the active deposit was decaying according to an exponential law, and corrections could be more conveniently applied, the activities of the strips in pairs, one from each side at the same distance from the bottom, were measured in a sensitive α-ray electroscope.

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[*] A. Debierne, *Comptes Rendus*, juin 1910, p. 1740.

[†] M. S. Leslie, *Comptes Rendus*, juillet 1911, p. 328.

[‡] A. Debierne, *Le Radium*, 1907, p. 213.

[§] Bruhat, *Le Radium*, 1909, p. 67.

[‖] S. Russ, Phil. Mag. xvii. p. 412 (1909).

Within the limits of experimental error the emanation ought to be distributed according to an exponential law * $p=p_0 e^{-\sqrt{\frac{\lambda}{D}}x}$, where p_0 is the initial concentration, p the concentration at a point at distance x, λ the radioactive constant, and D the coefficient of diffusion. If the active deposit reaches the plate at the level at which it is formed, the variation in the activity of the strips should follow the same law. This was not the case, however. The logarithm of the activities plotted against the distances x did not give a straight line but a curve, according to which the coefficient of diffusion apparently increased with the distance from the source.

Two parallel plates, 2 or 3 mm. apart, without a field, as in Debierne's and Bruhat's experiments with actinium emanation †, were then substituted, the distribution of emanation between them being examined; but still departures from an exponential law were observed. It was thought probable that this might be caused by the diffusion of some of the active deposit so that it reached the plates at a level other than that at which it was formed from the emanation. According to some observations made by Mme. Curie on radium deposit ‡, if the air containing emanation is not perfectly dry, agglomerations of molecules of water vapour and active deposit are probably formed. As the phenomenon observed might have been due to these, a tube of phosphorus pentoxide was placed in the cylinder to dry the air, but apparently a certain amount of disturbance still took place.

Next an electric field was employed § to direct the active deposit more rapidly to the plates. With 2–4 volts, and even with 40 volts, some trace of the same phenomenon remained; but with 80 volts practically a straight line was obtained when the logarithms of the activities were plotted against distance. In all subsequent experiments a difference

* Rutherford, 'Radioactivity,' p. 276.

† *Loc. cit.*

‡ Mme. Curie, *Comptes Rendus*, 1907, pp. 477 & 1145.

§ Rutherford, *loc. cit.*; Russ, *loc. cit.*

of potential of 160 volts was used. The measurements were begun about 1·5 cm. from the end of the cathode plate, and the strips of tinfoil did not extend the whole width of the plate, but were several millimetres shorter ; so that any effects due to non-uniformity of the field at the edge of the plate might be avoided. Measurements were made at atmospheric pressure, and also at reduced pressures. The product of the pressure P and the coefficient of diffusion D should be a constant at constant temperature, varying as the square of the absolute temperature. The values of P × D given below have been corrected for 15° C. The coefficient of diffusion was calculated assuming 54 seconds * as the period of transformation of thorium emanation, or $\lambda = 1{\cdot}29 \times 10^{-2}$ sec.$^{-1}$.

P.	P×D (corrected).	
76·2 cm.	6·31	at 80 volts
76·7 ,,	6·42	
75·8 ,,	6·07	
75·65 ,,	6·69	
75·5 ,,	6·00	
73·8 ,,	6·43	
54·95 ,,	6·74	
37·2 ,,	6·80	
31·2 ,,	6·89	
29·7 ,,	6·44	
12·8 ,,	6·20	
8·8 ,,	6·39	
Mean . .	6·46	

The value of D at 76 cm. pressure and 15° C. = ·085.

The apparatus was sufficiently long to prevent the necessity for additional corrections at reduced pressures.

Experiments with Actinium.—The thorium hydroxide was replaced by an actinium preparation, and the rate of diffusion determined in exactly the same way. All the experiments were made at reduced pressures, since at atmospheric pressure only a very small quantity of emanation reached the point at which the measurements were begun. An ordinary α-ray electroscope was used instead of the sensitive one employed in the experiments with thorium emanation. The period of transformation of actinium emanation † was taken as 3·9 secs. or $\lambda = 1{\cdot}8 \times 10^{-1}$ sec.$^{-1}$.

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* See note later.

† See note at the end.

P.	P×D (corrected).
42·75 cm.	7·50
42·0 „	8·30
36·95 „	6·80
33·25 „	7·40
32·5 „	6·77
20·7 „	7·23
19·9 „	7·50
18·2 „	6·82
17·45 „	7·87
15·9 „	7·25
15·7 „	7·44
Mean ..	7·44

The value of D in air at 76 cm. pressure and 15° C. = ·098.

Experiments with Glass Plates.—The values of the product P × D for actinium show even larger variations than those for thorium emanation. It was thought that perhaps the brass plates, about ·5 mm. thick, were not sufficiently rigid and that they did not always occupy the same relative positions. The measurements for actinium were therefore repeated, using glass plates 2 mm. thick, covered with tinfoil on the sides facing one another, except at the edges, which were left uncovered for insulating purposes.

P.	P×D (corrected).
43·75 cm.	8·57
39·8 „	8·17
34·35 „	8·04
32·55 „	8·23
27·25 „	7·70
25·0 „	8·07
22·2 „	7·94
17·6 „	7·95
14·35 „	8·41
11·85 „	7·87
Mean ..	8·12

The value of D in air at 76 cm. pressure and 15° C. = ·107.

Evidently the form of the apparatus has a considerable effect on the results.

If the value of P × D for thorium emanation is altered in the same degree, it should now be about 7·13. To test this point the determinations with thorium emanation were repeated, but with the difference that a small quantity of a strong radiothorium product was used instead of thorium hydroxide. Since the activities were not determined for at least five hours after the removal of the plates from the diffusion vessel, no difficulties would arise owing to the presence of radium emanation, because any radium active deposit would then have disappeared.

In the first experiments made the activities were eighty or ninety times those obtained in the former experiments, and the resulting value for P × D was found to be very high.

P.	P×D (corrected).	
77·1 cm.	8·63	exposures of 5 or 6 hours only.
77·1 „	10·48	
76·6 „	9·34	
76·6 „	8·70	
76·1 „	9·19	
76·0 „	8·29	
75·8 „	8·88	
Mean of last four ..	8·77	

The value of D in air at 76 cm. pressure and 15° C. = ·115.

The supply of emanation was cut down by covering the radiothorium with perforated tinfoil and layers of blotting-paper. The activities were now diminished to about twenty times those obtained from the hydroxide, and it was found that the value of P × D had also decreased.

P.	P×D (corrected).
76·7 cm.	8·76
76·0 „	8·15
76·0 „	8·48
75·9 „	8·21
75·9 „	8·17
75·8 „	9·38
Mean ..	8·51

The value of D in air at 76·0 cm. pressure and 15° C. = ·112.

A further diminution of emanation until it was only about five or six times that obtained from thorium hydroxide was again followed by a decrease in the value of the product P × D, but only to a slight extent.

P.	P×D (corrected).
76·7 cm.	8·58
76·5 „	8·42
76·3 „	8·54
76·0 „	8·58
76·0 „	8·92
75·8 „	8·49
75·5 „	8·36
75·0 „	8·11
75·0 „	8·07
42·0 „	9·02
26·7 „	8·06
16·0 „	8·05
Mean ..	8·43

The value of D in air at 76 cm. pressure and 15° C=·111.

Discussion of Results.—The results given are sufficient to show that apparently slight alterations in the form of the apparatus may produce considerable variations in the value of the diffusion coefficient as determined experimentally. The minor departures from constancy of the value P × D in experiments made with exactly the same apparatus and amount of emanation are probably due to slight deviations from parallelism of the plates. That other experimenters have found as great variations can be seen from the paper by Bruhat. He also gives a full list of his results, and deviations from the mean value to the extent of 14 or 15 per cent. may be noticed.

The experiments show further that even without any change in the apparatus it is possible to vary the value of D by varying the amount of emanation in the vessel. These two facts seem to indicate the reason, not only why, in the past, different experimenters have found different values for D, but also why there is a discrepancy between the observed and the calculated values. The disturbing cause is very probably the active deposit, a portion of which perhaps loses its charge by recombination with the ions in the air, and then behaves more or less as a gas, until it accidentally strikes one of the plates. The effect was naturally more pronounced where no field was employed, or only a single plate. Even when a field was employed the anode showed a small quantity of activity, about 5 or 6 per cent. of that on the cathode. This might have been due either to electrically neutral, or negatively charged particles. The portions of the active deposit producing the largest effect would be the long-period substances thorium B or actinium B. Indeed, ultimately it was only the amounts of thorium B and actinium B which were found, since, when the measurements were made, sufficient time had passed since the removal of the plates to allow all other products brought from the diffusion vessel to disappear. Wellisch and Bronson *, in a recent paper on the distribution of the deposit of radium in an electric field, have shown that with a difference of potential of 160 volts not more than 80 per cent. radium deposit reaches the cathode, and even with 4000 volts only 91 per cent. was obtained. This, it is true, was across a distance of 28 mm. and not 2 mm. as in the present experiments.

With an increase in the amount of emanation there will be an increase in the ionization. Hence, more reaction between the ions and the active deposits resulting in a greater value of D may reasonably be expected. This would account for the high values obtained with radiothorium as source of emanation. Wellisch and Bronson, in the paper just referred to, state that only with fields of a few volts does any change in the amount of deposit collected appear to follow a change in the degree of ionization. One might assume, however, that a neutral particle could collide with an ion and become charged again. In the experiments referred to, the final result would be the same as if the particle had remained charged all the time. This would not be the case, however, in the diffusion experiments, where it is important that the active deposit should attach itself to the plate at the level at which it is formed.

Evidently, it is exceedingly difficult to say when the thorium and actinium emanations may be justly regarded as comparable with one another. This may perhaps have been approximately the case when amounts of emanation which were equally active were employed, that is when the value of D for thorium emanation was ·111, and for actinium emanation ·107. If such an assumption were made, the results would indicate that the molecular weights are very close to one another. More reliance, however, could be placed on this conclusion if the periods of all the thorium products bore the same ratio to one another as those of the actinium products. The diffusion of the active deposits might then be expected to produce proportionately the same effect in each case.

With regard to the absolute value of the coefficient of diffusion, it may be concluded that the smaller values found are more nearly correct than the larger ones. The smallest

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* E. M. Wellisch and H. L. Bronson, Phil. Mag. May 1912 p. 714.

value was found for thorium emanation when only a very small amount of emanation was used, and when the plates were thin, *i. e.* metal plates ·5 mm. thick instead of the glass plates 2 mm. thick employed later. What is the exact effect produced by the thickness of the plate it would be difficult to say, but it seems reasonable to suppose that a thin plate in the diffusion vessel would produce less disturbance than a thick one. The value obtained under these circumstances was ·085. Therefore, one may say that at 76 cm. pressure and 15° C. the coefficient of diffusion of thorium emanation is not greater than, and may possibly be less than ·085. Similarly the upper limit for the coefficient of diffusion of actinium emanation is ·098.

Summary.

(1) The values found for the diffusion coefficients of the radioactive gases depend on the amount of ionization in the diffusion vessel, and on the arrangements made for collecting the active deposit.

(2) A comparison of the diffusion coefficients of thorium and actinium emanations under conditions as nearly identical as the differences of period of the different substances concerned will allow, indicates that the molecular weights of the two gases are probably very nearly equal.

(3) The real coefficients of diffusion of thorium and actinium emanations are not greater than, and probably less, than ·085 and ·098 respectively.

Note on the Periods of Transformation of Actinium and Thorium Emanations.

As a knowledge of the radioactive constants of the emanation is necessary for the calculation of the above results, it was thought desirable to employ values obtained by exactly similar methods. The decay of the emanations was followed directly by means of an electroscope.

In the first attempts made an emanation electroscope was partially evacuated, the leaf charged too much to be seen on the scale, and air containing a small amount of actinium emanation—not sufficient to drive the leaf entirely off the scale—was allowed to enter abruptly. After two or three seconds, when the leaf had appeared in the microscope, scale-readings were taken. The intervals of time were measured by means of a swinging pendulum placed near the electroscope, so that it could be watched at the same time as the scale was read. When the emanation had disappeared a continuation of the readings gave the leak. The activity due to the active deposit formed in the 25 or 30 seconds elapsing since the introduction of the emanation was practically zero. After corrections had been made for the leak and for variations in the sensitiveness along different parts of the scale, the difference between the final reading and the reading at any given moment would be proportional to the total amount of emanation present at that moment. The logarithms of these values were plotted against time. In nineteen experiments the values for the period varied between 3·70 and 4·00 seconds, giving a mean of 3·86 seconds.

In the hope of attaining a greater degree of accuracy a modification of the above method was devised. The pendulum was insulated and kept charged to a constant voltage, and as in swinging it passed its lowest point, it touched the exposed tip of a fine insulated wire passing from the gold-leaf support to the outside of the electroscope. Thus at definite intervals of time (about 2 seconds) the leaf could be re-charged, its fall representing the average activity of the emanation during that time. When no emanation was present, there was always a certain amount of oscillatory movement of the leaf, due partly to induction effects produced by the charged pendulum on the electroscope, and partly to the leak. Correction was made for this. In twelve experiments, of which five gave 3·95 seconds, the variation was between 3·90 and 3·98 seconds, the mean being 3·95 seconds.

A further change was then introduced. The outside of the electroscope was charged and the pendulum earthed. An earthed metal plate screened the electroscope from the pendulum except at the small hole through which passed the wire in connexion with the leaf. In this way all disturbance due to induced charges was prevented. Sixteen experiments gave values varying between 3·81 and 4·06 seconds, the mean being 3·92 seconds.

The period of thorium emanation was also determined by this method. Of twelve experiments eleven gave values varying between 53·5 and 55·1 seconds, mean 54·3 seconds: the twelfth, 55·8 seconds, varying considerably from the others, was neglected.

As the variations of the mean values from the period of 3·9 seconds found by Debierne [*] by the air-current method for actinium emanation, were much less than the variations between the actual experimental values obtained above, this value, 3·9 seconds or $\lambda = 1{\cdot}8 \times 10^{-1}$ sec.$^{-1}$ was retained in the calculation of the diffusion coefficient. Hahn and Sackur[*] obtained the same value by following the change of activity directly by means of an electrometer. Similarly the period of transformation, 54 seconds or $\lambda = 1{\cdot}29 \times 10^{-2}$ sec.$^{-1}$ found by Bronson[†], was adopted for thorium emanation.

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[*] Debierne, *Comptes Rendus,* 1904, p. 411.

My thanks are due to Professor Rutherford for his help and interest in these experiments.

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LXII. *The Ranges of the α particles from the Thorium and Actinium Products.* *By* H. Geiger, *Ph.D., Lecturer in Physics, and* J. M. Nuttall, *M.Sc., University of Manchester*[‡].

In two previous papers[§] we have shown that there exists a quantitative relation between the range of an α particle and the transformation constant of the product from which it arises. For the products of the uranium-radium series the values of the ranges of the α particles were partly taken from papers by Bragg[||], and were in part redetermined. As regards the members of the actinium and thorium series, with a few exceptions, only the initial measurements of Hahn[¶] were available.

A determination of the ranges of the α particles from most of the products of these families is difficult, since, owing to the short periods of some of them, it is impossible to separate the products from each other. Thus the actinium emanation and actinium A will always be associated with actinium X, and therefore complicate a determination of the range of the α particles from the latter substance. Similar difficulties arise in the thorium series.

In the following we have undertaken the redetermination of the ranges of the α particles emitted by the products of the thorium and actinium series, making use of the experimental arrangement we have previously employed for the determination of the ranges of the α particles from uranium.

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[*] Hahn and Sackur, *Ber. deutsch. Chem. Ges.* 38. ii. p. 1943 (1905).

[†] Bronson, Amer. Journ. of Sc. xix. p. 185 (1905).

[‡] Communicated by Prof. E. Rutherford, F.R.S.

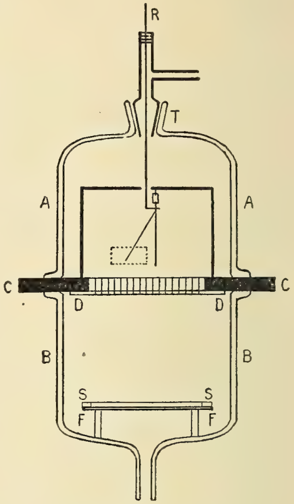
[§] H. Geiger and J. M. Nuttall, Phil. Mag. xxii. p. 613 (1911); xxiii. p. 439 (1912).

[||] W. H. Bragg and R. D. Kleeman, Phil. Mag. viii. p. 726 (1904); x. p. 318 (1905).

[¶] O. Hahn, Phil. Mag. xii. p. 244 (1906).

The apparatus, which is slightly modified, is shown again in fig. 1. The main part consists of two large bell jars AA and BB separated by a brass plate CC. A large number of holes—about 250—each 3·7 mm. in diameter and 8 mm. high, forming a circular "grid" of 10 cm. diameter, were drilled through the brass plate CC. An exactly similar but much thinner brass plate DD could be screwed on to the lower side of plate CC. Between these two plates a thin and uniform sheet of mica equivalent in stopping power to 1·1 cm. of air was placed, and fixed down air-tight. The lower bell-jar BB contained the active film FF at a distance 22·5 cm. from the mica. On account of the metal grid only the α particles emitted at angles less than 20° to the normal could pass through the mica into the upper bell-jar, which contained the electroscope. The latter was cylindrical in shape and was 8 cm. high and 10·5 cm. in diameter. It could be charged from outside through the wire R, which could be rotated by means of the ground-glass joint T. In the experiments the upper bell-jar was first completely exhausted and then filled with hydrogen up to a pressure of about 6 cm. of mercury. Hydrogen was used in preference to air, since, according to Taylor * and others, the rise of the ionization curve is more pronounced in the former gas than in the latter. When filled with hydrogen to 6 cm. pressure the depth of the ionization vessel corresponded to 1·6 mm. of air at atmospheric pressure, since the α particles had to travel through about 8 cm. in the electroscope before they were stopped by the upper plate. The ionization at different parts of the range of the α particles could be measured by varying the pressure in the lower bell-jar. In this way the ionization curves for the α particles from the different products were obtained.

Fig. 1.



The active materials were again deposited on ground-glass plates in exceedingly thin films. In order to prevent the escape of emanation into the bell-jar BB, which would have completely vitiated the experiments, the active film was covered with a thin and uniform sheet of mica attached to a

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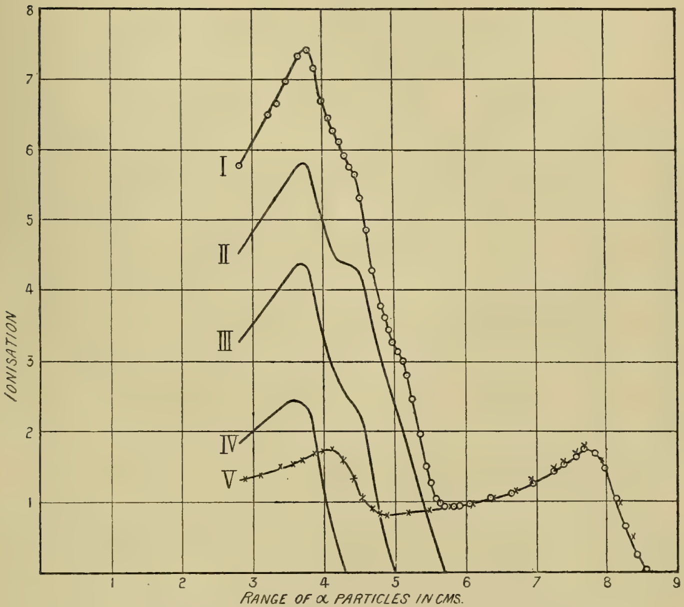
* T. S. Taylor, Phil. Mag. xviii. p. 604 (1909); xxi. p. 571 (1911).

ground-glass ring SS; the latter fitted air-tight over a ground-glass plate FF, thus forming a shallow circular box FSSF (see fig. 1), just large enough to hold the active film. A small hole was drilled through the centre of the glass plate FF to allow the gas to escape from the box when the pressure in the bell-jar BB was reduced. Since the glass plate on which the active matter was deposited and the plate forming the base of the box were in close contact no measurable amount of emanation could escape while measurements were taken, On account of the very slow escape of the gas from the box it was necessary to exhaust, and readmit the air, very slowly to prevent breakage of the mica.

Fig. 2.



Curve I. = α particles from Th X, Th Em., Th A, Th C_1, Th C_2.
II. „ „ Th X, Th Em., Th A.
III. „ „ Th X, Th Em.
IV. „ „ Th X.
V. „ „ Th C_1, Th C_2.

The thorium X was obtained from radiothorium, and a very thin film of high activity was prepared. Two days were allowed to elapse before measurements were taken, so that the active deposit might attain equilibrium with the thorium X. The ionization curve was then determined as described above, and is shown by Curve I. of fig. 2. To deduce the ranges of the products composing Curve I., Curve V. was first subtracted which represented the ionization produced by the α particles of the active deposit of thorium. This latter curve was obtained by a separate experiment, the results of which are represented by the crosses of Curve V. The difference curve, shown in Curve II., represents the ionization curve of the α particles from thorium X, thorium emanation, and thorium A. It was now necessary to analyse this latter curve into its three parts, due to the three types of α particles named above. This could be done by subtracting from Curve II. the ionization curve of a simple α ray product taken under exactly the same conditions. The accurate shape of the ionization curve of a simple α ray product could be taken from the long-range α particles of thorium C_2 from either of Curves I. or V. It had, however, to be borne in mind that the number of α particles from thorium C_2 is not the same as that from the other products. As Marsden and Barratt[*] have shown, thorium C_1 emits 35 α particles and thorium C_2 65 α particles for a hundred disintegrating atoms of thorium emanation. Moreover, on account of the fact that the period of thorium B is of the same order of magnitude as that of thorium X, there does not exist true radioactive equilibrium between these substances. Thorium B and the succeeding products will be present in excess of their true equilibrium values. From a simple calculation it is easy to show that the excess of thorium B over thorium X amounts to about 12 per cent.[†] On the other hand, thorium X, thorium emanation, and thorium A are for practical purposes in true radioactive equilibrium, *i. e.*, they emit the same number of α particles per second. By multiplying the ordinates of the end portion of Curve V. by the two factors $\frac{100}{65}$ and $\frac{88}{100}$ an ionization curve is obtained which, except for the range, must be identical with the curve for the separate α particles from thorium X, thorium emanation, or thorium A. This curve was subtracted twice from Curve II., making the ends of the ranges coincide in each case. The result of the first subtraction is shown in Curve III., giving the range of the thorium emanation. After the second subtraction, Curve IV. is obtained, which gives the range of the α particle from thorium X. Hence, finally, the horizontal distances from the origin at which the Curves II., III., IV. cut the axis of abscissæ give the ranges of the α particles from thorium A, thorium emanation, and thorium X respectively. The ranges are all compared with the range of thorium C_2 as standard (8·60 cm. at 15° C.). The ranges are tabulated in the table at the end of the paper, and are in fair agreement with the figures given by Hahn * and by Barratt †. The range of thorium X, which has not been determined before, was found to be 4·30 cm. at 15° C.

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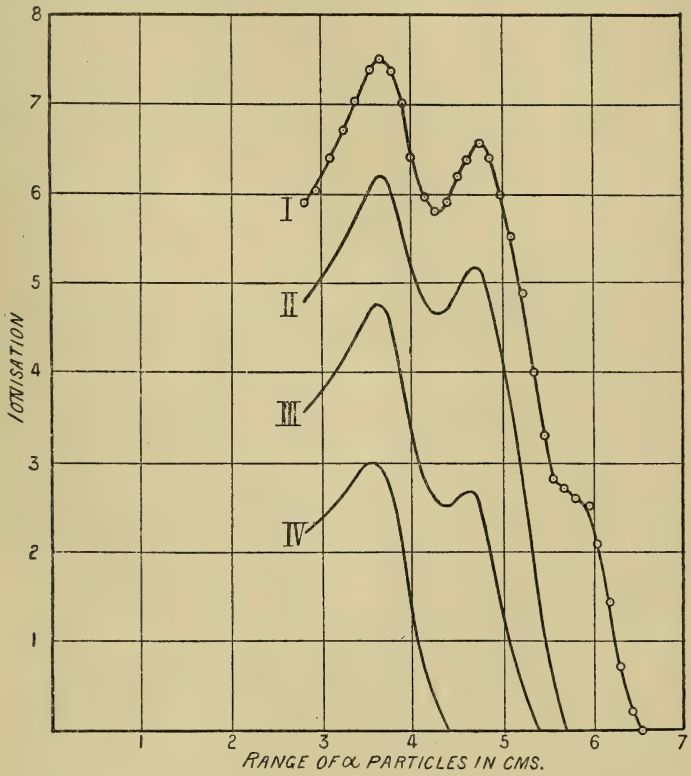
[*] E. Marsden and T. Barratt, Proc. Phys. Soc. xxiv. p. 50 (1911).

[†] Rutherford and Chadwick, Proc. Phys. Soc. xxiv. p. 141 (1912).

Fig. 3.



Curve I. = α particles from Act X, Act C, Act Em, Act A.
II. " " Act X, Act C, Act Em.
III. " " Act X, Act C.
IV. " " Act X.

Similar experiments were carried out with actinium X, under exactly the same conditions as described above in the case of thorium X. A very thin film of actinium X of sufficient activity was prepared. Curve I. of fig. 3 shows the

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* O. Hahn, Phil. Mag. xii. p. 82 (1906).

† T. Barratt, Proc. Phys. Soc. xxiv. p. 112 (1912).

experimental results, and gives the ionization curve of the α particles from actinium X, actinium C, actinium emanation, and actinium A. Since in this case there is no substance giving α particles of prominent range, it was more difficult to obtain the ranges of the different products by subtraction. The standard ionization curve was fitted on to the end of Curve I. (of fig. 3), so that the maximum coincided with the inflexion in Curve I. After subtracting the standard curve three times in succession, the ionization Curves II., III., IV. were obtained. Curve II. gives the ionization curve due to actinium X, actinium C, and actinium emanation; Curve III. that due to actinium X and actinium C; and Curve IV. that of actinium X. The Curve IV. finally remaining was slightly higher than the standard curve, but this deviation was probably within the experimental error. Since the period of actinium X is long compared with the periods of the succeeding products, no correction had to be made for the deviation from true equilibrium.

The ranges obtained from fig. 3 and given later in Table I. are in satisfactory agreement with the measurements taken previously by one of us * by the scintillation method, and also with those obtained by Hahn † by Bragg's method.

In our previous discussion of the ranges of the α particles from the actinium products we have taken for the range of the α particles from radioactinium the value obtained by Hahn, which is 4·80 cm., and slightly greater than that of actinium X. This result appears to be an exception to the relation we have given between range and period, since the α particles from actinium X, which has the shorter life, should have the longer range.

To decide whether this was actually an exception to the rule we have carried out experiments under exactly the same conditions with a film of radioactinium. This was prepared according to the method given by Hahn, and was at the time of measurement practically free from all subsequent products. The curve obtained indicated a value for the range little different from that found by Hahn, and showed that the α particles from radioactinium had actually a range somewhat longer than those from actinium X. The deviation from the range-period rule is perhaps only apparent, since it seems quite possible that radioactinium consists of two products, one of which emits β rays and has the period of about 19·5 days, and one which has a considerably shorter life and emits the α rays. Some preliminary

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* H. Geiger, Phil. Mag. xxi. p. 201 (1911).

† O. Hahn, Phil. Mag. xii. p. 244 (1906).

experiments to effect a separation have, however, so far been unsuccessful.

The following table gives the values of all the ranges of the α particles which have been given by us in this and previous papers. The values for radium emanation, radium A, and radium C are those given by Bragg and Kleeman. The ranges are given for the temperatures 0° C. and 15° C., and for convenience the initial velocities of expulsion of the α particles are added. The velocities v are calculated from the equation $v^3 = aR$, where R denotes the range of the α particles and a is a constant*. The initial velocity of the α particles from radium C is taken as $2{\cdot}06 \times 10^9 \frac{\text{cm.}}{\text{sec.}}$ †.

Ranges of α particles.

Substance.	Ranges at		Initial velocity.
	0° C.	15° C.	
Uranium 1	2·37 cm.	2·50 cm.	1·47 $10^9 \frac{\text{cm.}}{\text{sec.}}$
Uranium 2	2·75	2·90	1·54
Ionium	2·85	3·00	1·56
Radium..................	3·13	3·30	1·61
Ra Emanation	3·94	4·16	1·74
Radium A................	4·50	4·75	1·82
Radium C................	6·57	5·94	2·06
Radium F................	3·58	3·77	1·68
Thorium	2·58	2·72	1·51
Radiothorium	3·67	3·87	1·70
Thorium X	4·08	4·30	1·75
Th. Emanation.........	4·74	5·00	1·85
Thorium A	5·40	5·70	1·93
Thorium C_1	4·55	4·80	1·82
Thorium C_2	8·16	8·60	2·21
Radioactinium	4·36	4·60	1·80
Actinium X	4·17	4·40	1·77
Act. Emanation	5·40	5·70	1·93
Actinium A	6·16	6·50	2·02
Actinium C	5·12	5·40	1·89

In fig. 4 (p. 654) the logarithms of the transformation constants of the products are plotted against the logarithms of the ranges of the α particles. The relations for the uranium-radium and the actinium series have been given before, and are repeated with very slight changes. The points representing the products of the thorium series also lie approximately on a straight line which falls between and is parallel to, the corresponding lines for the radium and actinium series.

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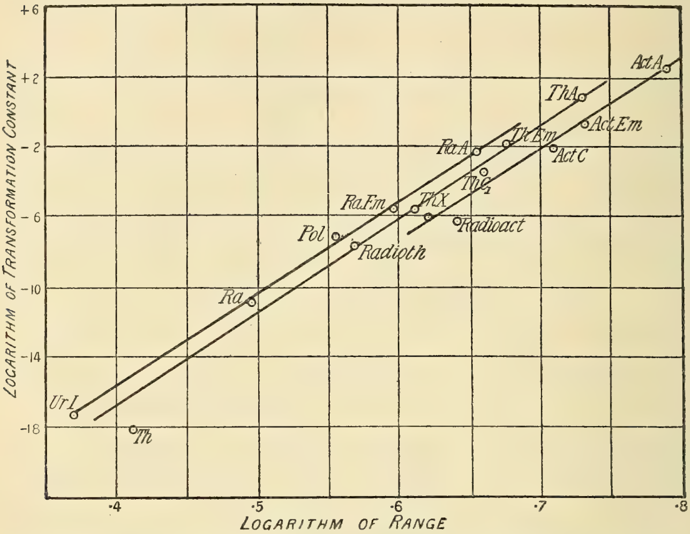
* H. Geiger, Proc. Roy. Soc. A. lxxxiii. p. 506 (1910).

† E. Rutherford, Phil. Mag. xii. p. 348 (1906).

Fig. 4.



The range of the α particles from thorium itself is somewhat longer than should be expected from the rule, but it must be remembered that this range is by far the most difficult to determine, since the activity from thorium alone is only about one-fifth of that from uranium. The deviation in this case may therefore be within the experimental error, and the only product which is not in agreement with the range-period rule is, as stated above, radioactinium, but there seems to be the possibility that this product has not the period which is usually attributed to it.

On account of the uncertainty of their periods the products uranium 2, ionium, radium C, and thorium C_2 are not entered on fig. 4. From the straight line relation it follows that uranium 2 should have a period about 2×10^6 years and ionium a period of about 200,000 years. The latter figure is of the same order as the approximate value given by Soddy*, namely, 132,000 years. The periods of radium C and thorium C_2 should be about 10^{-6} second and 10^{-11} second respectively.

We wish to express our thanks to Prof. Rutherford for his kind interest in these experiments.

The Victoria University, Manchester,
Physical Laboratories.

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* F. Soddy, *Le Radium*, vii. p. 295 (1910).

LXIII. *On the Emission of Sound by a Source on the Axis of a Cylindrical Tube.* *By* Mary Taylor, *M.Sc. (Manchr.)**.

THE following problem was suggested by Lord Rayleigh in his 'Theory of Sound,' Art. 301. It is here worked out; and attention is drawn to a point of some interest. It appears that the emission of energy by the source is a *discontinuous* function of the frequency. If the frequency be supposed to be gradually increased, the emission tends to become infinite as the frequency approaches any one of a series of critical values, but becomes finite again *immediately* on passing these. This is on the hypothesis of no dissipative forces. An attempt is also made to show the manner in which such forces will affect the above results.

First consider the case of an incompressible fluid. The motion is evidently symmetrical about the axis of the cylinder. Hence, using cylindrical coordinates r, θ, z, the origin being at the position of the source, and the axis of z along the axis of the cylinder, the equation of motion, which is satisfied at all points except the origin, is

$$\frac{\partial^2\phi}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial\phi}{\partial r}+\frac{\partial^2\phi}{\partial z^2}=0, \quad . \quad . \quad . \quad . \quad (1)$$

ϕ being the velocity potential.

Considering only that part of the cylinder which lies on the positive side of the plane $z=0$, assume that ϕ varies as e^{-kz}, the minus sign being taken to insure finiteness at infinity. The equation (1) then becomes

$$\frac{\partial^2\phi}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial\phi}{\partial r}+k^2\phi=0. \quad . \quad . \quad . \quad . \quad (2)$$

The most general solution of (2) which is finite for $r=0$, is $\phi=\mathrm{A}\mathrm{J}_0(kr)\,.\,e^{-kz}$, in the notation of Bessel's functions. The condition of zero normal velocity over the surface of the cylinder gives

$$\mathrm{J}_0'(ka)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a is the radius of the cylinder. Thus the complete solution of (1) applicable to the present case is

$$\phi=\mathrm{A}z+\Sigma\mathrm{A}_s\mathrm{J}_0(k_sr)e^{-k_sz}, \quad . \quad . \quad . \quad . \quad (4)$$

where the summation extends over all values of k_s, other than zero, which satisfy (3).

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* Communicated by Prof. H. Lamb, F.R.S.

The constants A and A_s are to be determined from consideration of the flux across the section $z=0$. Over this section $\partial\phi/\partial z$ will clearly vanish except for $r=0$, but the total flux across it must be $\frac{1}{2}$, the strength of the source being taken to be unity. Hence we must have

$$\int_0^a \left(-\frac{\partial\phi}{\partial z}\right)_{z=0} 2\pi r\, dr = \tfrac{1}{2}. \quad . \quad . \quad . \quad . \quad (5)$$

Now, from (4), by the conjugate property of Bessel's functions,

$$\int_0^a \left(-\frac{\partial\phi}{\partial z}\right)_{z=0} J_0(k_s r)\, 2\pi r\, dr = k_s A_s \int_0^a \{J_0(k_s r)\}^2 2\pi r\, dr$$

$$= \pi a^2 k_s A_s \{J_0(k_s a)\}^2, \quad . \quad (6)$$

in virtue of the equation (3)*.

But

$$\int_0^a \left(-\frac{\partial\phi}{\partial z}\right)_{z=0} J_0(k_s r)\, 2\pi r\, dr = \int_0^a \left(-\frac{\partial\phi}{\partial z}\right)_{z=0} 2\pi r\, dr = \tfrac{1}{2},$$

since $(-\partial\phi/\partial z)_{z=0}$ vanishes except for infinitesimal values of r. Hence

$$A_s = \frac{1}{2\pi a^2 k_s \{J_0(k_s a)\}^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and similarly

$$A = -\frac{1}{2\pi a^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Hence

$$\phi = \frac{1}{2\pi a^2}\left[-z + \Sigma \frac{J_0(k_s r) e^{-k_s z}}{k_s\{J_0(k_s a)\}^2}\right]. \quad . \quad . \quad . \quad (9)$$

For large values of z the first term in this solution is preponderant, and $-\partial\phi/\partial z$ assumes approximately the constant value $1/2\pi a^2$.

Next consider the case when the fluid is gaseous. The equation of motion now is

$$\frac{\partial^2\phi}{\partial t^2} = c^2\nabla^2\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where c is the velocity of sound in the fluid. If ϕ varies as

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* Rayleigh, 'Theory of Sound,' § 203.

e^{ikct}, this becomes

$$\nabla^2\phi + k^2\phi = 0; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or, with the same coordinates as before,

$$\frac{\partial^2\phi}{\partial r^2} + \frac{1}{r}\frac{\partial\phi}{\partial r} + \frac{\partial^2\phi}{\partial z^2} + k^2\phi = 0. \quad . \quad . \quad . \quad (12)$$

Considering only that part of the cylinder which lies on the positive side of the plane $z=0$, we assume that ϕ varies as $e^{-m_s z}$. The equation (12) then becomes

$$\frac{\partial^2\phi}{\partial r^2} + \frac{1}{r}\frac{\partial\phi}{\partial r} + k_s^2\phi = 0, \quad . \quad . \quad . \quad . \quad (13)$$

where

$$k_s^2 = k^2 + m_s^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The most general solution of (14) satisfying the conditions of the problem is found, in the same manner as before, to be

$$\phi = \left[\frac{1}{2\pi ika^2}e^{-ikz} + \Sigma\frac{J_0(k_s r)e^{-m_s z}}{2\pi a^2 m_s\{J_0(k_s a)\}^2}\right]e^{ikct}, \quad . \quad (15)$$

where the summation extends over all values of k_s which satisfy the equation

$$J_0'(k_s a) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Two cases arise in this problem according as the values of m_s are or are not all real. First suppose k to be less than the least value of k_s (other than zero) which satisfies (16); that is to say, we assume the period of the disturbing force to be greater than that of the gravest mode of free radial vibrations. The values of m_s are then all real, and the solution, written in real form, is

$$\phi = \frac{1}{2\pi a^2}\left[\frac{\sin k(ct-z)}{k} + \Sigma\frac{J_0(k_s r)e^{-m_s z}\cos kct}{m_s\{J_0(k_s a)\}^2}\right]. \quad . \quad (17)$$

For large values of z the disturbance reduces practically to the system of plane waves,

$$\phi = \frac{1}{2\pi ka^2}\sin k(ct-z). \quad . \quad . \quad . \quad . \quad (18)$$

The energy transmitted per unit time across unit area of the wave front is then $\rho c/8\pi^2 a^4$, and the rate of emission of energy by the source is therefore $\frac{\rho c}{4\pi a^2}$. The rate at which energy is emitted by a unit source in free space is $k^2c\rho/8\pi$; so that the presence of the cylindrical wall alters the total emission of energy in the ratio $2/k^2a^2$.

Next suppose that the period of the forced vibrations is less than the pth free period but greater than the $(p+1)$th, so that the first p values of $m_s{}^2$ are negative, say $m_s{}^2=-\mu_s{}^2$. The solution (15) may then be written

$$\phi=\left[\frac{1}{2i\pi ka^2}e^{-ikz}+\sum_1^p\frac{\mathrm{J}_0(k_sr)e^{-i\mu_sz}}{2\pi a^2i\mu_s\{\mathrm{J}_0(k_sa)\}^2}\right.$$

$$\left.+\sum_{p+1}^{\infty}\frac{\mathrm{J}_0(k_sr)e^{-m_sz}}{2\pi a^2m_s\{\mathrm{J}_0(k_sa)\}^2}\right]e^{ikct}; \quad . \quad (19)$$

or, in real form,

$$\phi=\frac{\sin k(ct-z)}{2\pi ka^2}+\sum_1^p\frac{\mathrm{J}_0(k_sr)\sin(kct-\mu_sz)}{2\pi a^2\mu_s\{\mathrm{J}_0(k_sa)\}^2}$$

$$+\sum_{p+1}^{\infty}\frac{\mathrm{J}_0(k_sr)e^{-m_sz}\cos kct}{2\pi a^2m_s\{\mathrm{J}_0(k_sa)\}^2}; \quad . \quad . \quad . \quad (20)$$

so that the disturbance no longer reduces to a plane wave for large values of z.

Now suppose that the forced period is only very slightly less than the pth free period, so that μ_p is very small. The term into which this quantity enters will then be very great, and will tend to infinity as μ_p tends to zero. The velocity potential will of course also tend to infinity as the forced period approaches coincidence with a free period from a slightly greater value. There is, however, a remarkable difference between the emission of energy in the two cases.

The energy given out by the source is obtained by integrating $-p\partial\phi/\partial z$ over the section of the cylinder, where p denotes the pressure of the fluid. Remembering that $p=p_0+\rho\partial\phi/\partial t$, where p_0 denotes the undisturbed pressure and ρ the density, the mean value of the energy emitted per unit time is readily found from equation (20) to be

$$\frac{\rho c}{8\pi a^2}+\sum_1^p\frac{\rho kc}{8\pi a^2\mu_s\{\mathrm{J}_0(k_sa)\}^2}.$$

Thus, if the forced period is only slightly less than the pth free period, so that μ_p is very small, the expression for the energy emitted becomes very great and tends to infinity as μ_p tends to zero. If, however, the forced period is slightly greater than the pth free period, the energy expression is

$$\frac{\rho c}{8\pi a^2}+\sum_1^{p-1}\frac{\rho kc}{8\pi a^2\mu_s\{\mathrm{J}_0(k_s a)\}^2},$$

and is finite. Thus the emission of energy is discontinuous for values of the forced period coinciding with a free period; viz., it tends to a finite or infinite limit according as the critical period is approached from a higher or a lower value.

If we had started on the supposition that the period of the source is coincident with one of the free periods, say $k=k_p$, we should have found

$$\phi=\frac{1}{2\pi ka^2}\sin k(ct-z)+\left\{\mathrm{A}-\frac{z}{2\pi a^2\{\mathrm{J}_0(ka)\}^2}\right\}\mathrm{J}_0(kr)\cos kct$$
$$+\sum_1^{p-1}\frac{\mathrm{J}_0(k_s r)\sin(kct-\mu_s z)}{2\pi a^2\mu_s\{\mathrm{J}_0(k_s a)\}^2}+\sum_{p+1}^{\infty}\frac{\mathrm{J}_0(k_s r)e^{-m_s z}\cos kct}{2\pi a^2 m_s\{\mathrm{J}_0(k_s a)\}^2}, \qquad (21)$$

where A is arbitrary. The rate of emission of energy is therefore

$$\frac{\rho c}{8\pi a^2}+\sum_1^{p-1}\frac{\rho k_p c}{8\pi a^2\mu_s\{\mathrm{J}_0(k_s a)\}^2},$$

which is the same as the limit to which the emission tends as the forced period approaches coincidence with the pth free period from a slightly greater value.

The reason why the emission of energy is very great when the forced period is slightly less than the free period, but not when it is slightly greater, is found in the difference in the relationship between the phases of the pressure and velocity in the two cases. When the forced period is slightly the smaller, the very large term in the expression for the pressure is in the same phase with the corresponding term in the velocity, and is therefore in a condition favourable for doing work. But as k increases through a root of $\mathrm{J}_0'(k_s a)=0$, the important term in the expression for $\partial\phi/\partial t$ undergoes a change of phase of a quarter period, and thus differs in phase by this amount from the corresponding velocity. Thus it does no work on the whole.

It is obvious that in any actual case the discontinuities noticed above cannot occur; and the problem therefore needs some modification in the case of approximate isochronism. This is effected by the introduction of dissipative forces of the nature of friction, viscosity, or heat conduction, which have hitherto been neglected. They are in fact, as a rule, unimportant except in the critical cases. The simplest hypothesis which we can make in the present problem is that the motion of the particles of the fluid is resisted by a frictional force proportional to the absolute velocity. This is of course not the true law of friction, but it will serve to indicate the kind of modification which dissipative forces will introduce.

If u, v, w are the component velocities at a point in the fluid, parallel to coordinate axes of x, y, z, the equations of motion become

$$\rho\frac{\partial u}{\partial t}=-\frac{\partial p}{\partial x}-\mu' u, \text{ \&c., \&c.,} \quad . \quad . \quad . \quad (22)$$

and the equation of continuity is

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}+\frac{\partial s}{\partial t}=0, \quad . \quad . \quad . \quad . \quad (23)$$

where s denotes the "condensation." Again, if the loss of heat by radiation and conduction be neglected, we have

$$p=p_0+c^2\rho s. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Now suppose that u, v, w, s, and p all vary as e^{ikct}. We have, then,

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}+ikcs=0, \quad . \quad . \quad . \quad . \quad (25)$$

while the equations (22) become

$$(\rho ikc+\mu')u=-\frac{\partial p}{\partial x}, \text{ \&c., \&c.,} \quad . \quad . \quad . \quad (26)$$

or, if $\mu'=\rho\mu$,

$$\rho(ikc+\mu)u=-\frac{\partial p}{\partial x}, \text{ \&c., \&c.} \quad . \quad . \quad . \quad (27)$$

Differentiating the equations (27) with respect to x, y, z in order, and adding, we get

$$\rho(ikc+\mu)\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)=-\nabla^2 p=-c^2\rho\nabla^2 s, \quad (28)$$

which, combined with (25), gives

$$\rho ikcs(ikc+\mu)=c^2\rho\nabla^2 s,$$

or

$$(\nabla^2+h^2)s=0,$$

provided

$$h^2=k^2-\frac{ik\mu}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The equations (27) will be satisfied by

$$u=-\frac{\partial\phi}{\partial x},\quad v=-\frac{\partial\phi}{\partial y},\quad w=-\frac{\partial\phi}{\partial z},\quad . \quad . \quad . \qquad (30)$$

provided

$$\phi=\frac{c^2 s}{ikc+\mu}=-\frac{ikcs}{h^2}\quad . \quad . \quad . \quad . \quad . \quad . \qquad (31)$$

Thus ϕ must satisfy the equation $(\nabla^2+h^2)\phi=0$, or, with the same coordinates as before,

$$\frac{\partial^2\phi}{\partial r^2}+\frac{1}{r}\frac{\partial\phi}{\partial r}+\frac{\partial^2\phi}{\partial z^2}+h^2\phi=0. \quad . \quad . \quad . \quad . \qquad (32)$$

Assuming ϕ to vary as $e^{-m_s z}$, the typical solution of (32) is

$$\phi=\mathrm{A}\mathrm{J}_0(k_s r)\,e^{-m_s z}\,e^{ikct}, \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

where

$$k_s^2=m_s^2+h^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

The condition of zero normal velocity over the surface of the cylinder gives as before

$$\mathrm{J}_0'(k_s a)=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (35)$$

Thus the solution of (32) which is appropriate to a positive progressive wave, and gives the correct value for the flux across the section $z=0$, is

$$\phi=\left[\frac{e^{-ihz}}{2i\pi h a^2}+\Sigma\frac{e^{-m_s z}\,\mathrm{J}_0(k_s r)}{2\pi a^2 m_s\{\mathrm{J}_0(k_s a)\}^2}\right]e^{ikct}. \quad . \quad . \qquad (36)$$

Now write $m_s=\alpha_s+i\beta_s,\quad ih=\alpha+i\beta, \quad . \quad . \quad . \quad . \quad . \qquad (37)$

whence

$$\alpha_s^2-\beta_s^2=k_s^2-k^2,\quad 2\alpha_s\beta_s=k\mu/c,\quad \alpha^2-\beta^2=-k^2,\quad 2\alpha\beta=k\mu/c, \quad . \quad . \quad . \quad . \qquad (38)$$

Substituting from (37) in (36) we get for the value of ϕ in real terms

$$\phi=\frac{e^{-\alpha z}\{\alpha\cos(kct-\beta z)+\beta\sin(kct-\beta z)\}}{2\pi a^2(\alpha^2+\beta^2)}$$

$$+\Sigma\frac{e^{-\alpha_s z}\{\alpha_s\cos(kct-\beta_s z)+\beta_s\sin(kct-\beta_s z)\}\mathrm{J}_0(k_s r)}{2\pi a^2(\alpha_s^2+\beta_s^2)\{\mathrm{J}_0(k_s a)\}^2}. \qquad (39)$$

The values of α_s and α found from (38) must of course be taken with the positive sign, to insure finiteness at infinity. It is easily seen that in the case of no friction when $\mu=0$, the above result reduces to that previously obtained.

Now suppose that the period of the forced vibration coincides with one of the periods of free radial vibration in the case of no friction, say $k=k_p$. Then $\alpha_p=\beta_p=\surd(k\mu/2c)$, and the corresponding term in the velocity potential, expressed as a real quantity, is

$$\frac{e^{-\surd(k\mu/2c)z}J_0(kr)\{\cos(kct-\surd(k\mu/2c)z)+\sin(kct-\surd(k\mu/2c)z)\}}{4\pi a^2\surd(k\mu/2c)\{J_0(k_s a)\}^2}. \quad . \quad . \quad . \quad . \quad (40)$$

This is finite, even in the case of isochronism, though it tends to infinity as μ tends to zero.

To find the energy emitted by the source we must take the integral of the expression $-p\partial\phi/\partial z$ over the cross-section $z=0$. We find, from (36)

$$-\left(\frac{\partial\phi}{\partial z}\right)_{z=0}=\frac{1}{2\pi a^2}\cos kct+\Sigma\frac{J_0(k_s r)\cos kct}{2\pi a^2\{J_0(k_s a)\}^2}. \quad . \quad (41)$$

Also $$p=p_0+c^2\rho s=p_0+\rho(ikc+\mu)\phi.$$

Hence
$$(p)_{z=0}=p_0+\rho\mu\left[\frac{\alpha\cos kct+\beta\sin kct}{2\pi a^2(\alpha^2+\beta^2)}+\Sigma\frac{J_0(k_s r)(\alpha_s\cos kct+\beta_s\sin kct)}{2\pi a^2(\alpha_s^2+\beta_s^2)\{J_0(k_s a)\}^2}\right]$$
$$+\rho kc\left[\frac{\beta\cos kct-\alpha\sin kct}{2\pi a^2(\alpha^2+\beta^2)}+\Sigma\frac{J_0(k_s r)(\beta_s\cos kct-\alpha_s\sin kct)}{2\pi a^2(\alpha_s^2+\beta_s^2)\{J_0(k_s a)\}^2}\right]. \quad . \quad . \quad . \quad . \quad (42)$$

Hence the mean value of the energy emitted per unit time is

$$\frac{\rho\mu\alpha}{8\pi a^2(\alpha^2+\beta^2)}+\frac{\rho kc\beta}{8\pi a^2(\alpha^2+\beta^2)}+\Sigma\frac{\rho(\mu\alpha_s+kc\beta_s)}{8\pi a^2(\alpha_s^2+\beta_s^2)\{J_0(k_s a)\}^2}. \quad . \quad . \quad . \quad . \quad (43)$$

If the forced period differs only slightly from the pth free period, so that $k_p^2-k^2$ is small, we can write

$$\alpha_p^2-\beta_p^2=k_p^2-k^2=\pm\epsilon_p^2, \quad . \quad . \quad . \quad . \quad (44)$$

the upper or lower sign being taken according as the forced or free period is the greater. Also

$$2\alpha_p\beta_p=k\mu/c.$$

Hence

$$\alpha_p^{\,2}+\beta_p^{\,2}=\left\{\frac{k^2\mu^2}{c^2}+\epsilon_p^{\,4}\right\}^{\frac{1}{2}}$$

$$\left.\begin{aligned}\alpha_p&=\frac{1}{\sqrt{2}}\left\{\left(\frac{k^2\mu^2}{c^2}+\epsilon_p^{\,4}\right)^{\frac{1}{2}}\pm\epsilon_p^{\,2}\right\}^{\frac{1}{2}},\\ \beta_p&=\frac{1}{\sqrt{2}}\left\{\left(\frac{k^2\mu^2}{c^2}+\epsilon_p^{\,4}\right)^{\frac{1}{2}}\mp\epsilon_p^{\,2}\right\}^{\frac{1}{2}},\end{aligned}\right\}\quad .\ .\ .\quad (45)$$

The part of the emission due to the *p*th term of the sum in (43) is

$$2\cdot\frac{1}{8\pi a^2\{\mathrm{J}_0(k_pa)\}^2}\cdot\frac{\mu\left\{\left(\frac{k^2\mu^2}{c^2}+\epsilon_p^{\,4}\right)^{\frac{1}{2}}\pm\epsilon_p^{\,2}\right\}^{\frac{1}{2}}+kc\left\{\left(\frac{k^2\mu^2}{c^2}+\epsilon_p^{\,4}\right)^{\frac{1}{2}}\mp\epsilon_p^{\,2}\right\}^{\frac{1}{2}}}{\left\{\frac{k^2\mu^2}{c^2}+\epsilon_p^{\,4}\right\}^{\frac{1}{2}}},$$

or, writing $\mu/kc=\nu$, $\epsilon_p/k=x$,

$$\frac{\rho}{\sqrt{2}}\cdot\frac{c}{8\pi a^2\{\mathrm{J}_0(k_pa)\}^2}\cdot\frac{\nu\,.\,\{(\nu^2+x^4)^{\frac{1}{2}}\pm x^2\}^{\frac{1}{2}}+\{(\nu^2+x^4)^{\frac{1}{2}}\mp x^2\}^{\frac{1}{2}}}{\{\nu^2+x^4\}^{\frac{1}{2}}}.\quad .\ .\ .\ .\quad (46)$$

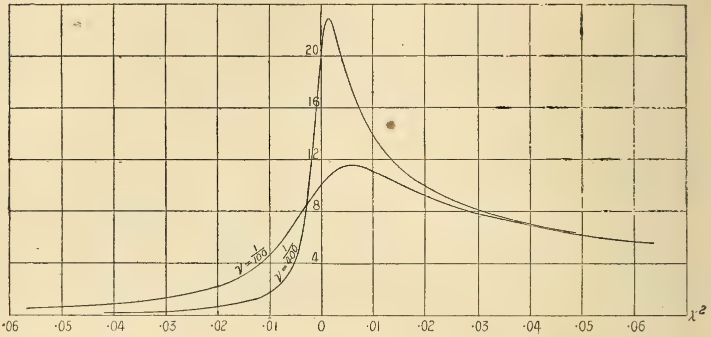
As the forced period tends to coincidence with a free period, ν being supposed to have a definite value, this expression tends to the limit

$$\frac{\rho}{\sqrt{2}}\cdot\frac{c}{8\pi a^2\{\mathrm{J}_0(ka)\}^2}\cdot(\nu^{\frac{1}{2}}+\nu^{-\frac{1}{2}}),$$

whichever of the two periods was originally the greater. Thus the discontinuity which occurred in the case of no friction does not now present itself.

This problem is interesting as furnishing an instance of a "double limit." If in the expression (46) we make first x and then ν tend to zero, that is to say, if we make the periods tend to coincidence and then make the friction vanish, the expression tends to an infinite limit. If, however, we make ν vanish before x, the limit to which the expression tends is zero or infinite, according as the upper or lower sign is taken, that is according as the forced or free period is originally the greater.

The accompanying diagram shows the variation of the last factor in the expression (46) as a function of x^2. In the lower of the two curves the value of ν has been taken to be 1/100, and in the higher 1/400. The left-hand side of the figure corresponds to the upper sign in (46), that is to say, to the case when the forced period is slightly greater than the free period. The more abrupt descent on this side of the figure, of the curve for which ν has the smaller value,



shows how the discontinuity which occurs in the case of no friction is approached as the friction diminishes.

It is to be noted that the maximum value of the expression (46) does not occur when the forced period exactly coincides with the free period, but for a slightly smaller value, the difference between the two values diminishing as the friction is diminished.

LXIV. *Note on a Ruler for Drawing Curves.*

By The Earl of Berkeley, *F.R.S.*[*]

It is well known that by bending a steel ruler so as to cover five experimental points, a fair approximation to the true curve may be obtained, thereby affording a ready means of interpolation. Should high accuracy be required, it is often best to plot the known points on an extended scale, the steel ruler then becomes extremely difficult to manipulate: to obviate this, some two or three years ago I devised the ruler here described. Fig. 1 gives a plan of the apparatus as set up to draw a curve through the five points marked with a cross—the dimensions of the parts are to the scale given on the plan, but it may be mentioned that for the highest accuracy a curve on a larger scale is advisable.

A and B are two metal T squares cut out of sheet "duralumin." The two claws C and D (shown in plan and

[*] Communicated by the Author.

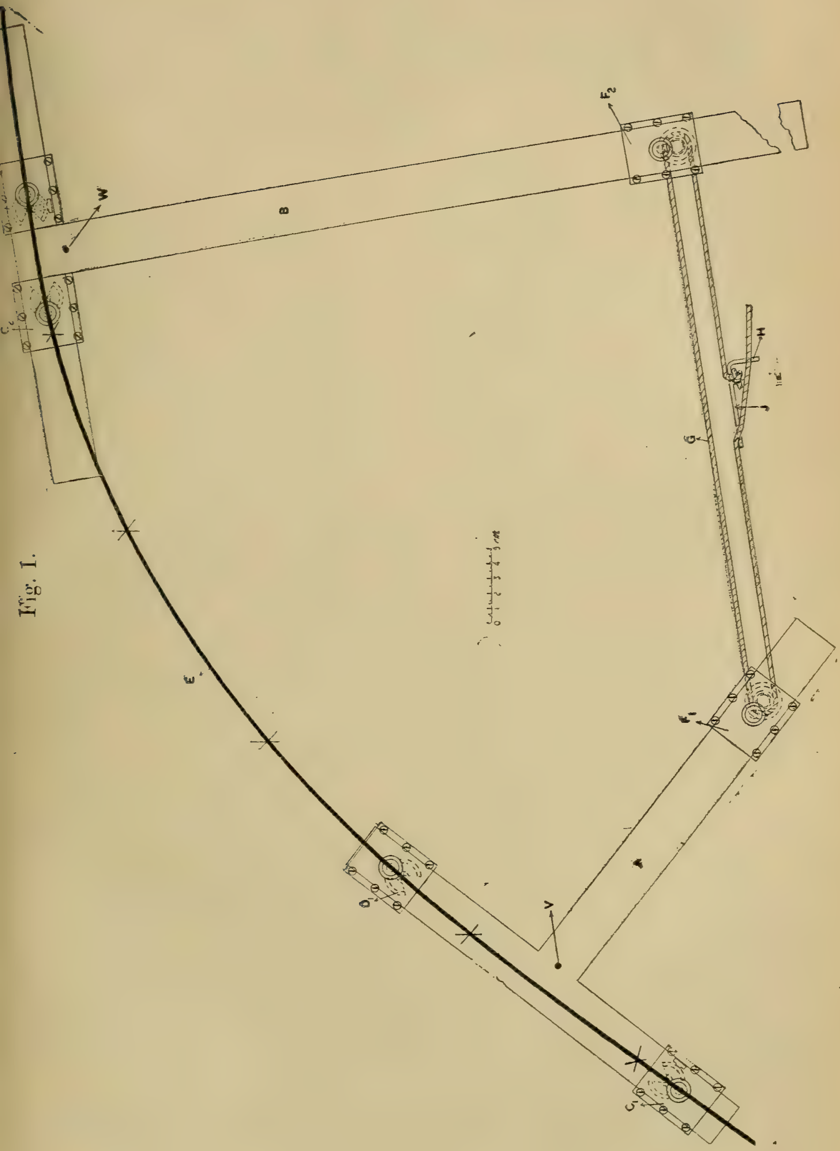
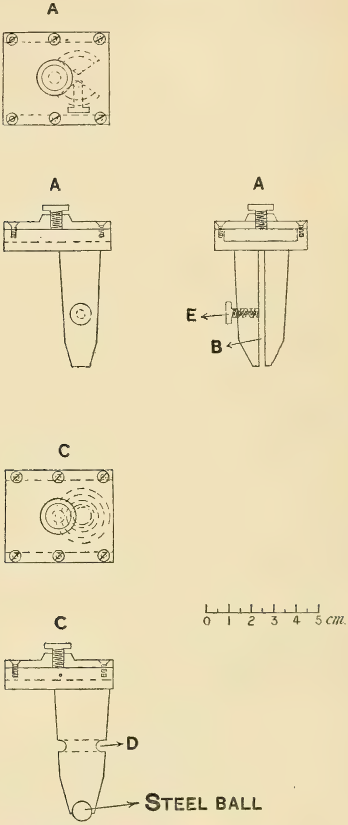


Fig. I.

two elevations under A in fig. 2) slide on either end of the short arms of the T's and hold a Chesterman steel ruler (1·5 metres long, 5·7 cm. wide. and 2·4 mm. thick) in the jaws* B of fig. 2. The pins F† (plan and elevation under D of fig. 2) slide on the long arms of the T's; they are pulled towards each other by the cord G which passes round the grooves D of fig. 2—this cord is "belayed" by pulling it tight into a V-shaped slot cut at H in the brass right-angled piece J.

Fig. 2.



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* It may be of use to mention that these jaws were made by putting two saw cuts, with a circular saw, through the solid pin at right angles to one another and parallel to the vertical axis.

† In actual construction the T with the longer arm has that arm set high so as to clear the other T should it be necessary for them to cross—hence one of the pins is made longer so as to avoid "wringing" the ruler.

It is evident that the slope of the tangent to the ruler at a point can be given almost any value by altering the tension on the cord, while the curvature can be altered both by varying the relative positions of the claws and pins on their arms and by bringing the heads of the T's closer together or further apart—in fact, the practical limit to the variation in curvature lies in the physical properties and thickness of the steel.

In general, if the curvature change sign, the ruler, as the apparatus is at present constructed, cannot be made to follow the curve—an exception to this is afforded by a point of inflexion near the end of the curve; here, as will readily be seen, if the pin F_1 (fig. 1) be slid towards the ruler to such a position that the line F_2F_1, produced, cuts the T anywhere between the two claws, a movement in a clockwise direction is set up round C_1, thus giving a point of inflexion.

If the curve begins as a straight line it may be necessary to substitute a hook in place of the set screw E (fig. 2), and pass the cord over this.

Theoretically the ruler should be so adjusted that the curve to be drawn comes between D_1 and C_2, thus avoiding any slight changes of curvature that there may be at these points, but in practice I have found for curves of moderate curvature that this effect is not noticeable.

As a test, a curve of the natural sines plotted against the corresponding angles was drawn on a scale such that 1° of the abscissæ = 7·5 cm., while 0·1 of the ordinates = 5 cm. The following *four* points were taken as known—0°, 18°, 72°, and 90°; and a curve was drawn through them, giving for the values of the natural sines of 36° and 54° the number ·595 instead of ·588, and ·813 instead of ·809, respectively. An objection may be raised against this test in that a uniform steel ruler, when its ends are pulled together by a small force, must give a sine curve; the validity of this objection is greatly lessened when it is realized that the forces required to get the steel to give the curve, on the scale mentioned, were so great that the ruler was permanently and largely deformed.

Opportunity was taken to test this deformed ruler against a logarithmic curve, by passing it through the logs (to the base 10) of the numbers 1, 2, 4, 8, and 10, on a scale such that 7·5 cm. = ·075 in the logs and 1 in the numbers. The interpolated value for the log of 6 was ·7810, instead of ·7782.

The actual value of the apparatus lies not so much in enabling one to draw curves such as these, but in getting smooth graphs on an extended scale. For instance, suppose we have obtained the densities (assumed correct to 1 in 50,000) of five solutions of widely different concentrations, and these be plotted on squared paper 100 cm. by 75 cm.; on passing the ruler through the points, interpolation values will be obtained which, when tested by experiment, will be found to be only 1 or 2 parts in 10,000 out.

In a case such as this it would seem that theoretically the accuracy obtainable is limited chiefly by the unavoidable errors in the paper (errors of ruling and of "stretch") and in the quality of the ruler. It is found, however, that a practical limit is imposed by the weight of the apparatus; for, with the 1·5 metre ruler, the ease of adjustment is already interfered with by the friction between the steel edge and the paper. This difficulty may be overcome by attaching vertical rods to the T's underneath the points V and W (fig. 1), so that by the aid of springs the ruler is held a millimetre above the surface of the paper, but can be depressed into contact by pressure. The lower end of the rods terminates in a steel ball which slides on the polished surface of three others above it, but rolls on the paper; this device is found to be a very efficient unlubricated castor.

LXV. *Multiply-charged Atoms.*

By Sir J. J. Thomson, *O.M., F.R.S.*[*]

[Plate XV.]

IN the photographs of the positive rays (see, for example, those given in the Phil. Mag. Aug. 1912) the mercury line is remarkable for the exceptionally small displacement of the head of its parabola. Even when the electric and magnetic fields are strong enough to produce deflexions of several millimetres in the heads of the parabolas corresponding to the other elements, the head of the mercury parabola is so little deflected that at first sight it seems to coincide with the origin. When, however, the electric field used to deflect the particles is made very large, in our experiments from 5000 to 10,000 volts per centimetre, the head of this parabola is distinctly displaced, and on measuring the electrostatic displacement it is found to be 1/8 of the normal displacement of the heads of the parabolas corresponding to the other elements.

The displacement due to the electric field is inversely proportional to the kinetic energy of the particle displaced, so that the atoms which produce the head of the mercury parabola must have eight times the maximum amount of energy possessed by the normal atoms. This could be accounted for if some of the mercury atoms in the discharge-tube had lost 8 corpuscles, for then the energy communicated to the atom by the electric field would be eight times the energy communicated to an atom with the normal charge. Eight is a very large number of corpuscles to lose, much larger than the number lost by the other elements which get multiple charges. I had previously to these experiments never found a case in which this number exceeded three; so that in my paper in the Phil. Mag. for August 1912, I suggested another explanation of the behaviour of the mercury line. A study of the plates taken with large electrostatic deflexions has revealed the existence of 7 parabolas due to mercury, corresponding to the mercury atom with 1, 2, 3, 4, 5, 6, 7 charges respectively, the parabola corresponding to 8 charges has not been detected, but as the parabolas get in general fainter for each additional charge on the atom, it is probably there but too faint to be detected. Pl. XV. fig. 1, taken from a photograph when the gas in the tube was the residual gas left after exhaustion by the Gaede pump, shows these lines very well. The measurements of *m/e* for these parabolas gave the following values:—

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[*] Communicated by the Author. Read before the Mathematical Congress at Cambridge, August 26, 1912.

m/e.	
200	
102	200/2
66·3	200/3
50·4	200/4
44	this not a mercury line but is due to CO_2.
39·8	200/5
33·7	200/6
28·6	200/7

It will be noticed that the heads of the parabolas corresponding to 1, 2, 3 charges respectively lie on a straight line passing through the origin, indicating that the velocities of the particles producing the heads of these parabolas are all equal, and therefore, since each particle is an atom of mercury, that the kinetic energy of the particles at the heads of the parabolas is constant. This is what we should have expected, for the heads of all the parabolas are due to particles which had originally lost 8 corpuscles, the particle at the head of the parabola corresponding to one charge has regained 7 of these after passing through the cathode, that at the head of the parabola corresponding to two charges, six, and so on; these particles when in the discharge-tube were all in the same condition, and so acquired the same amount of kinetic energy.

The question now arises as to how the mercury atom acquires these very various charges. When a mercury atom is ionized, can it lose any number of corpuscles from one to eight? Taking for example a mercury atom with 5 positive charges, has it got into this condition by losing 5 corpuscles when it was ionized, or did it originally lose the maximum number 8 and regain 3 subsequently? The photographs prove, I think, that the second supposition is the correct one, and that in the discharge-tube there are two, and only two, kinds of ionization; in one of these kinds the mercury atom loses 1 corpuscle, while in the other kind it loses 8, and that there are no indications of ionization of such a character as to deprive the mercury atom of 7, 6, 5, 4, 3, or 2 corpuscles.

The evidence for this is as follows: let us suppose for a moment that atoms with any charge from 1 to 8 were produced by the ionization of the mercury atoms in the discharge-tube. Consider now the parabola due to the mercury atom which, when it passed through the electric and magnetic fields, had one positive charge. This parabola would result from atoms of the following kinds:—

1. Atoms which had lost 8 corpuscles on ionization and regained 7;
2. Atoms which had lost 7 and regained 6;
3. Atoms which had lost 6 and regained 5,

and so on, the eighth and last members of the series being atoms which had lost one corpuscle on ionization and had not regained it.

The parabola on the photographic plate would be due to the superposition of the 8 parabolas due to these types of atoms.

If $8d$ is the horizontal distance from the vertical axis of the head of the parabola due to the atom which lost one corpuscle on ionization, the horizontal distances of the heads of the parabolas due to atoms of the 1st, 2nd, 3rd types will be respectively $8d/8$, $8d/7$, $8d/6$, $8d/5$, $8d/4$, $8d/3$, $8d/2$, $8d$. Thus up to the horizontal distance $8d/7$ there would be only one parabola, at $8d/7$ another parabola would be added, this would produce an abrupt increase in the intensity of the photograph, there would be another abrupt increase at $8d/6$, another at $8d/5$, and so on. Thus the intensity of the parabola on the photograph would not be continuous, there would be places where the intensity was suddenly increased giving a beaded appearance to the photograph. The abrupt increase at $8d$ is very marked on this parabola, the others are not visible; but as the intensity of this parabola is very great it might be thought that they escaped detection owing to the breadth of the parabola. Let us therefore consider one of the finer parabolas, say, that due to the atom with four charges, to which this objection does not apply.

This parabola might arise from atoms which had lost 8 charges on ionization and regained 4, from those which had lost 7 and regained 3, and so on, the last being atoms which had lost 4 and not regained any. Then if d has the same meaning as before, the horizontal distances from the vertical axis of the heads of the parabola would be $4\times 8d/8$, $4\times 8d/7$, $4\times 8d/6$, $4\times 8d/5$, $4\times 8d/4$; there would, therefore, be abrupt increases in intensity at $32d/7$, $32d/6$, $32d/5$, $32d/4$. The photographs show, however, that the intensity is perfectly continuous, and not one of these abrupt increases is to be seen. We conclude, therefore, that there are no atoms which begin with 7, 6, 5, 4, 3, 2 charges, and that in this case there are two and only two types of ionization, in the one type an atom loses a single corpuscle, in the other it loses 8.

This result suggests that ionization takes place in the discharge-tube in two ways. In the first method the ionizing agents are the rapidly moving corpuscles which constitute the cathode rays, these very small particles penetrate into the atom and come into collision with the corpuscles inside it individually, the collision in favourable cases causing the corpuscle struck to escape from the atom; this type of ionization results in the atom losing a single charge. In the other type of ionization we suppose that the mercury atom is struck by a rapidly moving atom and not by a corpuscle; after the collision the mercury atom starts off with a very considerable velocity, which at first is not shared by the corpuscles inside it. The tendency of the corpuscles to leave the atom depends only upon the *relative* velocity of the atom and the corpuscles inside it, so that the ionizing effect produced by the collision is the same as if the atom were at rest, and *all* the corpuscles were moving with the velocity acquired by the atom in the collision. Thus if there were eight corpuscles in the mercury atom connected with about the same firmness to the atom, the result of the atom acquiring a high velocity in a collision might be the detachment of the set of eight leaving the atom with a charge of 8 units of positive electricity. We see in this way how the cathode particles might produce one type of ionization resulting in singly charged atoms, while the atoms forming the positive rays might produce another type of ionization resulting in multiply-charged atoms.

All the elements I have examined give multiply-charged positive atoms with the exception of hydrogen, on which I have never observed more than one charge; in no other case, however, have I observed charges approaching that possessed by mercury. The majority of the elements seem to acquire only two charges; this is the number acquired by helium, and this case is interesting since in the vacuum-tube the helium atom occurs with both single and double charges, whilst as an α particle it always seems to have two charges, suggesting that the process by which the α particle acquires its charge is analogous to the process by which multiply-charged atoms are produced in the discharge-tube.

I have observed nitrogen atoms with three charges, but the parabola due to the triply-charged atom is exceedingly faint. Argon shows triply-charged atoms very distinctly as can be seen from fig. 2, where the parabolas I, II, III due to Arg_{+}, Arg_{++}, Arg_{+++} are all very distinct; the Arg_{++} parabola has probably a parabola due to neon superposed on it.

This plate shows the helium line, and thus incidently gives us an estimate of the sensitiveness of this method of detecting small quantities of a gas. The volume of the discharge-tube was about two litres, the pressure 1/300 of a mm. of mercury: there was thus in the discharge-tube about 1/100 c.c. of argon at atmospheric pressure. This is about the amount in 1 c.c. of air at this pressure, and as the helium line was visible along with the argon, we see that this method can detect the amount of helium in 1 c.c. of air, which, according to Sir William Ramsay, is about 4×10^{-6} c.c., even though this is mixed with an enormous excess of argon. The tube used for this photograph was not at all well adapted for detecting small quantities of an impurity, as the cathode had been in use for several weeks and the tube through it was almost silted up by the sand-blast action of the positive rays, and was just about to be replaced by a new tube.

An interesting result, which is now being investigated, is that when very pure nitrogen is in the discharge-tube the mercury line corresponding to the atom with five charges becomes abnormally bright, brighter than those for the atom with four or even three charges, though in other gases the greater the charge on the atom the fainter the line.

I have much pleasure in thanking Mr. F. W. Aston, B.A., Trinity College, for the great assistance he has given me in these investigations.

LXVI. *Resonance Spectra of Iodine by Multiplex Excitation.* *By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University* *.

[Plates XVI.–XIX.]

IN a previous paper (this journal, Oct. 1911) I have described the general nature of the resonance spectra of iodine excited by the light of the mercury arc, and the remarkable transformation of the simple resonance spectrum into the complicated band spectrum produced by collisions of the iodine molecules with molecules of gases of the helium group. In the course of a very extended study of resonance spectra with which I have been engaged off and on for the past seven years, I have come to the conclusion that no very great advance could be made until some method was devised for varying the wave-length of the exciting light by very small amounts.

In the previous work the spectra excited by a large number of widely separated wave-lengths have been studied, but no very general conclusion as to the nature of the molecular mechanism could be drawn from the accumulated material.

During the past winter I have advanced a step in the right direction, and have made a very good beginning on the work which I have always hoped would be possible.

Some very astonishing results have been obtained which throw a good deal of light on certain points that I never felt able to explain in the course of the work on sodium vapour.

I have found, for example, that the resonance spectrum of iodine is quite different when excited by the green line of the Cooper-Hewitt mercury lamp (commercial glass lamp), from the resonance spectrum excited by the *same line* from the mercury arc in quartz (high temperature arc): in other words, the resonance spectrum suffers profound changes when small changes occur in the structure of the exciting line. In all of the previous work I have assumed that only one of the hundreds of absorption-lines was operated upon by the exciting line, though in one or two cases I ventured the hypothesis that in some cases the exciting line might be broad enough to act upon two absorption-lines simultaneously. (See paper by R. W. Wood and F. E. Hackett on the resonance spectra of sodium photographed with the concave grating, Astro-physical Journal, vol. xxx. No. 5, 1909.)

The complexity of the iodine absorption spectrum has been greatly underestimated. With any grating of moderate power it appears to be completely resolved, though some of the lines appear broader than others. I find, however, that with every increase in the resolving power that I bring to bear, more structure comes into view.

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* Communicated by the Author.

The elaborate maps and tables of wave-lengths which have been published from time to time are absolutely worthless. I have made a study of this absorption spectrum only in the vicinity of the mercury emission-lines which I have employed for exciting the resonance spectra, but this study has demonstrated what I have for many years suspected, that tables of wave-lengths of spectra of this type are of no more value than a carefully prepared table of the weights of the individual grains in a cupfull of sand.

I have employed the highest resolving power that has ever been brought to bear upon the spectrum, and it is still not completely resolved. As an illustration of the amount of value to be attached to tables of wave-lengths and maps, I may mention that I have found seven sharp and cleanly resolved absorption-lines of iodine *within* the green mercury line emitted by the quartz mercury arc. This group of seven lines is represented by a single line only on Hasselberg's great map of the iodine spectrum. Fourteen absorption-lines were found in one of the yellow mercury lines and twelve in the other. When, therefore, we excite the resonance spectra by one or the other of these lines, from seven to fourteen different frequencies may respond to what we might be tempted to call monochromatic excitation.

It becomes at once clear why a small change in the distribution of the intensity in the exciting line or in its structure may modify the resonance spectrum.

Excitation by lines which are broad enough to excite a number of adjacent frequencies I have accordingly named *multiplex excitation,* to distinguish it from excitation by lines so narrow that they cover a single absorption-line only. I have even succeeded in modifying the line structure of the exciting line by the use of ray filters which remove certain frequencies from it: for example, by passing the green light from the mercury arc through bromine vapour before allowing it to enter the iodine vapour, we can produce a change in the resonance spectrum excited by the green mercury line. The changes produced in this way are very interesting, and the same method could without doubt be applied to the study of the resonance spectra of sodium, by filtering the light through iodine or bromine vapour before allowing the selected line to stimulate the vapour of sodium.

In my earlier paper I expressed the belief that much more could be learned from the study of the resonance spectra of iodine than was the case with sodium, since the vapour is much easier to handle. This belief has been amply justified, and I have so improved the method of investigation that I can now secure with an exposure of ten minutes a far better photograph of the resonance spectrum than was obtained with an exposure of 24 hours in the first experiments which I made in collaboration with Dr. Franck in Berlin in 1910.

I shall first take up the subject of the resonance spectra as a whole, photographed with my large three-prism spectrograph, and then pass to the more interesting subject of the structure of the resonance lines themselves as affected by the structure of the exciting line. This part of the work was done with the concave grating. The study of the absorption of the iodine for the frequencies falling within the spectral range covered by the exciting lines, owing to their finite width, was done first with a six-inch plane grating in the fourth order spectrum, used in conjunction with a spectrometer of considerably over two metres focus, and subsequently with a 40-foot spectrograph which I installed at my East Hampton laboratory in August of the present year.

Apparatus and Methods.

Thus far I have employed only the mercury arc for the excitation of the vapour, for I have found that sufficient variety could be obtained with this source alone to make possible a very complete study of the genesis of resonance spectra. It has, moreover, an advantage over most other sources of monochromatic light in that it is extremely brilliant, and can be kept running continuously for an almost indefinite length of time. I have employed two different types of lamp: a commercial Cooper-Hewitt, burning in a long glass tube at a comparatively low temperature, and a very powerful Westinghouse Cooper-Hewitt lamp (quartz) such as is used for the sterilization of water on a large scale. This lamp is of almost insupportable brilliancy, and many times more powerful than the small Heraeus lamps with which I have worked previously. I have already had it in operation over 2000 hours, and so far as I can see it is in as good order as when first made. It operates at 220 volts and takes 7 amperes when first started, the current dropping gradually during the first ten minutes of operation, becoming stationary at about 3·5 amperes, the lamp then being red-hot. I had my lamp constructed so that it could be used end-on if necessary, which has proved advantageous in the case of another investigation with which I have been occupied. The lamp is mounted in a large wooden box, furnished with a number of apertures, so that two or three investigations can be made with it simultaneously. Over one of these apertures is fitted a large lantern condenser 25 cm. in diameter, which forms an image of the mercury arc along the axis of the tube containing the iodine vapour. I find it advantageous to make these tubes rather larger than those which I used at first. I now make them about 40 cm. long and 4 or 5 cm. in diameter, with one end blown out into a bulb 6 cm. in diameter. It is important to get this bulb as clear and free from striæ as possible, and above all things not to have a drop of glass at the centre. This can be accomplished by drawing out the tube sideways in closing it preliminary to blowing it out. The other end of the tube is drawn down to a diameter of about 5 mm., and a thick-walled constriction made close to the large tube for sealing after exhaustion. Before making the constriction a few small crystals of iodine are introduced into the tube, which is then put in communication with a Gaede or other mercurial pump and thoroughly exhausted. I usually keep the Gaede pump in operation for ten minutes, as the gas passes but slowly through the capillary at low pressures. The tube is used end-on of course, the iodine vapour being highly luminous along the axis of the tube where the image of the horizontal mercury arc is focussed. The intensity can be further increased by means of a strip of looking-glass placed close to the wall of the tube, which reflects the rays back through the vapour. In some cases I have silvered the outer surface of the iodine tube along the side opposite to that through which the rays enter. This acts as a concave cylindrical reflector and focusses the rays back again at the centre of the tube. If it is desired to stimulate the vapour by the light of the Cooper-Hewitt arc in glass, the same tube can be used mounted alongside of the lamp and as close to it as possible, no lens being used. The entire mass of iodine vapour within the tube becomes luminous, though the intrinsic intensity is much less than with the quartz arc, perhaps one third as great. The mirror should of course be used in this case.

The iodine tube was brought close up to the slit of the spectrograph, no lens being used on account of the large size of the luminous spot. The resonance spectra were photographed with a prism spectrograph furnished with three very large flint-glass prisms (12 cm. high) and a Cooke portrait-lens of about 1 metre focus. Higher dispersion was obtained by photographing the spectra with a concave grating of 2 metres radius of curvature, very bright in the first order, ruled with 15,000 lines to the inch. The absorption spectrum was studied visually in the fourth order spectrum of a six-inch plane grating with the large spectrometer previously mentioned. The resolving power was 300,000, and the grating easily separated lines only 0·03 Ångström units apart. Photographs were made with this grating, but they did not show as much fine detail as could be observed visually and measured with the eyepiece micrometer, on account of small tremors which are never wholly absent in Baltimore, even late at night.

The fine groups of absorption-lines of iodine which fall within the range covered by the green and two yellow emission-lines of the mercury arc were first observed and studied with a large echelon grating, but subsequent work with the large plane grating showed that the results yielded by the echelon had been wrongly interpreted, owing to the overlapping of different orders, and they will not be further discussed, as it was at once apparent that a six-inch plane grating in the fourth order spectrum gave equal resolving power, sharper definition, and results about the interpretation of which there could be no doubt. In each case the spectrum of a neon tube was photographed on the same plate superposed on the resonance spectrum, the length of the slit being reduced, however, to make their identification certain. In some cases the iron arc was impressed upon the plate as well, as the neon tube gives but few lines in the green region, while very rich in lines in the yellow, orange, and red. In the case of the grating photographs the comparison spectrum was not superposed on the resonance spectrum, the usual method of a rotating slot being employed.

The 40-*foot Spectrograph.*

The discovery of the satellite lines which accompany the resonance lines, and the change in their position and intensity which resulted from changes in the distribution of the intensity within the exciting line, made a careful photographic study of the absorption spectrum of the iodine and of the emission spectrum of the mercury arc much to be desired. I accordingly fitted up during the past summer a plane grating spectrograph of 12·5 metres focal length. As this spectrograph appears to be, with the possible exception of Professor Michelson's ten-inch grating instrument, the largest and most powerful in the world, a description of the method of mounting may be of interest. The grating is a plane one ruled by Dr. Anderson on the 15,000 machine, and the photographs which I have taken with it of the iodine absorption spectrum show that it yields its full theoretical resolving power of 300,000 in the fourth order, which is bright enough to yield a fully exposed photograph of the solar spectrum with a very fine slit in three minutes, when used with a lens of 12·5 metres focus. My laboratory at East Hampton is in an old barn of very large size, and as temperature differences and striæ due to air-currents can be better avoided by having the entire apparatus under cover, I first mounted the apparatus in the building. I soon found, however, that vibrations of the building due to wind, and probably expansion and contraction of its frame due to the changing position of the sun, made it very difficult to secure satisfactory photographs, though I occasionally obtained one showing full theoretical resolving power. I finally determined to mount the instrument entirely independent of the building, supporting the grating and the lens on a cast-iron pier outside of the building, and the slit and plate-holder on a similar pier sunk in the ground just inside the wall of my dark-room. Not wishing to order a lens until I had tried out the instrument under the conditions prevailing at East Hampton (I had some fear of vibrations resulting from the surf on the beach a quarter of a mile distant), I borrowed, through the courtesy of Professor Campbell and the regents of the University of California, a very fine six-inch achromatic lens of 40-foot focus. The pier, which carried this lens and the grating, I improvised from two six-inch water mains which were slightly damaged by last winter's frost, and were to be had for the asking. The joints of these pipes had been ground together, and the two were bolted together as when laid for service. The resulting pipe was sunk to a depth of six feet in the ground, and a triangular brass bracket from my junk heap, which had originally formed a truss on an old fashioned support for a large reflecting telescope, was bolted to a bent piece of wrought iron, which was in turn bolted to the flange on the top of the water-pipe. The cell of the lens was fastened to the brass triangle with adjusting screws in the usual manner. The grating was mounted on a circle taken from a discarded spectrometer, which was turned by a worm gear. A bevel gear, removed from a discarded hand-drill, was fastened to the worm, the small gear-wheel being turned by a long rod, made by fastening four lengths of cheap brass-covered iron curtain rod together. This rod passed through the wall of the barn, terminating in a wheel a little to one side of the plate-holder and slit. When photographing with the apparatus, the small gear-wheel is thrown out of mesh with the large one by sliding a wooden support through which the rod passes a little to one side, the object being to prevent the transmission of vibrations from the grating-house and the long wooden tube to the grating support. The wooden tube, down which the light from the slit passes to the lens and grating and back again to the plate or eyepiece, was supported on posts and roofed over to prevent it from being heated by the sun. The end of the tube passes through the wall of the grating-house, but does not come in contact with the lens support. The plate-holder and slit were supported on a shorter piece of water-pipe, which passed through the floor of the laboratory without contact with it. The camera consisted of two wooden boxes, one sliding within the other (for focussing), joined to the end of the long tube with black cloth, which shut out the light but did not transmit vibrations. The long tube was made by nailing eight-inch boards together, and was painted black on the inside. Some trouble was given by spiders, which built their webs at intervals along the tube, a difficulty which I surmounted by sending our pussy-cat through it, and subsequently destroying the spiders with poisonous fumes.

The grating-house was built with double walls, and shingled on the outside, the shingles being nailed to wooden strips so as to leave an air-space between them and the roof. The iron pier was shielded from the wind by a wooden box built around it, which reached from the ground to the seven-inch hole in the floor of the grating-house, through which the pier passed without contact.

I have mentioned these details of construction to show that a somewhat elaborate apparatus can be put together out of odds and ends, without going to the expense of castings and machine-work. Photographs of the entire structure, and the top of the pier and the grating and lens supports, before they were housed in, are reproduced on Plate XIX.

The apparatus has proved satisfactory in every way, the only trouble resulting from air currents, which blow down the tube and stir-up striæ. These give no trouble at night, and are practically absent on calm days, but on windy days with hot sunshine they impair the definition somewhat. The rest of the equipment which I installed for the work consisted of a heliostat for work with sunlight, and a Cooper-Hewitt mercury rectifier, which delivers 3·5 amperes at 220 volts for operating the mercury lamps. While this spectroscope does not equal in resolving power the most powerful echelons and plane-parallel plates, I am of the opinion that the perfection of the grating, the circumstance that it is very bright in the fourth order, and the long focus of the lens, make it second to no other instrument in the world capable of yielding a continuous spectrum. Lines in the bromine absorption spectrum separated by a distance of only ·022 of an Ångström unit are clearly separated in the photographs, while the theoretical resolution is ·018 A.U.

The Absorption Spectrum.

The absorption spectrum of iodine is made up of a large number of fluted bands, and resembles in its general appearance the channelled absorption of sodium vapour, for in both cases the bands at the long wave-length end are quite regular in their appearance, while at the short wave-length end they become more or less confused. As I have already said, the number of absorption-lines which collectively form the banded spectrum of iodine has been greatly underestimated. Sunlight from the heliostat was passed through a large exhausted bulb containing a few small crystals of iodine and focussed upon the slit of the instrument. The absorption spectrum seen with the large spectrograph presented a most wonderful appearance, nearly the entire visible spectrum being filled with thousands of lines. As I have said, I found seven sharp and beautifully resolved lines within the green emission-line of mercury. The total width of the line was 0·4 A.E., and we have at this rate eighteen lines to the Ångström unit, or about 36,000 lines in all. There were, however, groups containing lines much closer together than the seven lines just enumerated, which were still unresolved by the grating, and numerous broad dark bands undoubtedly made up of unresolved lines. This circumstance, together with the fact that the lines are much closer together in the red, orange, and yellow region, makes me feel certain that there are upwards of 50,000 lines in this remarkable absorption spectrum.

The wave-lengths of the seven lines which were observed within the green mercury line (furnished by the quartz mercury arc) were very carefully measured with the eyepiece micrometer, with reference to the wave-lengths of the components of the mercury line seen with a low-temperature arc. They were subsequently measured from photographs taken with the 40-foot spectrograph, with reference to the main component of the green mercury line, which bisects absorption-lines 3 and 4, and the wave-length of which is 5460·7424.

The wave-lengths of the seven iodine absorption-lines are as follows :—

5460·966
·910
·873
·768
·716
·640
·579

As will be seen presently, the resonance spectra ought to be studied under equally high resolving power, but this is almost out of the question, on account of the comparative feebleness of the light. I have, however, obtained excellent photographs with a concave grating of six feet radius of curvature, and hope to do better in the autumn.

The examination of the absorption spectrum under the highest dispersion possible is of interest in connexion with the finite width of the lines due to the velocities of the molecules in the line of sight. They are at their best only when the iodine vapour is in a very high vacuum : the presence of air, even at rather low pressure, causes the lines to lose in sharpness, and eventually obliterates the finer ones.

A portion of the absorption spectrum 8 Ång. units in width is reproduced on Pl. XVIII. spectrum W, in coincidence with the corresponding portion of the spectrum from Hasselberg's map, enlarged to the same scale. The three broad lines on my photograph are solar lines, which appear on Hasselberg's map immediately above his spectrum. Hasselberg's map was prepared by hand from his table of measurements made from photographs taken with a grating of inferior power, the drawing being subsequently verified by comparison with the photograph. A comparison of the two shows that the lines in Hasselberg's map mean nothing at all, except that they indicate roughly the position of some of the groups of lines. A study of these two pictures cannot but furnish food for thought to astronomers working at the problem of the canals on Mars.

The group of seven lines which fall within the green mercury line are enclosed with a bracket, and when it is remembered that the entire portion of the spectrum reproduced embraces a range of the spectrum not much greater than the distance which separates the D lines of sodium, the frightful complexity of these absorption spectra becomes evident.

I have examined the absorption spectrum of sodium with this very powerful apparatus, and find that it is equally complex, the distance between the lines being about the same as in the case of iodine. Sodium, however, exhibits only a single faint line within the green mercury line, and as this appears only when the vapour has a considerable density, the mercury arc is incapable of stimulating this vapour to appreciable fluorescence.

The bromine absorption spectrum is reproduced in coincidence with that of iodine on the same plate (spectrum V). Further reference will be made to this when I come to the subject of the use of bromine vapour as a ray filter for modifying the intensity distribution in the green mercury line, and for the present I shall only draw attention to the somewhat suggestive circumstance that a large number of the lines in the two spectra coincide. From a rather hasty study of the original plate with a low power microscope (the photographs reproduced are threefold enlargements), I have come to the conclusion that there are more coincidences than can result from accident, a question which can doubtless be settled by the study of a wider range of the spectrum and a count of the percentage of coincidences with the spectra thrown out of wave-length coincidence by varying amounts. It appears to me that there may very possibly exist in the two elements identical systems of electrons, which give rise to similar frequencies in the two molecules. This is a point which I am studying at the present time.

It may be well to point out that the iodine absorption spectrum observed with sunlight is far superior to the solar spectrum for testing large gratings.

The Resonance Spectra.

As I have indicated in previous communications, the resonance spectrum of the iodine vapour, excited to luminosity by the light of the mercury arc, consists of three superposed series of nearly equidistant lines, one excited by the green line, the other two by the yellow lines. I have succeeded in separating the former from the two latter by the interposition of suitable absorbing screens between the mercury lamp and the iodine tube, and in the discussion of the results I shall take up the series separately.

If we photograph the resonance spectra with a spectrograph giving fairly high dispersion we find that the lines which form the series excited by the green line are in reality close doublets, accompanied by fainter companions, which however do not appear except on fully exposed plates. Neglecting these companions for the present, we will consider the series of doublets. The extent of this series has been somewhat extended since the earlier investigation, and it now consists of twenty-five members (all double), two of which are missing. Some of the others are very faint. Certain lines were found to be missing in the case of the resonance spectra of sodium vapour, and this peculiarity is probably characteristic of all resonance spectra. Dunoyer has made the suggestion that each line in the series originates from a special configuration of an aggregate of two or more sodium atoms or aggregates of sodium and the residual gas in the tube, and that the missing lines correspond to aggregates which are unstable or which cannot exist. This is an interesting hypothesis, and we are at once reminded of the equilibrium figures formed by floating magnets, some of which are very unstable, while others cannot exist at all.

My first idea regarding the series of doublets was that a close pair of absorption-lines were excited by the green line, and that the spacing of the lines in the two series thus originated was slightly different, the two series starting at the same point (the green mercury line). This would, however, give us a series of doublets with constantly increasing separation, whereas the observed separation is very nearly constant (about 2 Ångström units). The law governing the spacing of the doublets is not the same as that which obtains in the case of the resonance spectra of sodium, in which case I have found that the lines are spaced at very nearly equal distances along a normal spectrum. This makes the wave-length differences constant, but the law is by no means strictly followed, and matters become only worse if we take frequency differences. In the case of iodine the distance between the lines increases steadily as we pass towards the region of longer wave-lengths, but if we take the frequencies, or what amounts to the same thing, the reciprocals of the wave-lengths, we find that the frequency differences are *approximately constant. They are not strictly so however, and it seems possible that the departures may be the result of slight perturbations which modify the periods.

The wave-lengths were determined from photographs made on Wratten and Wainwright films, with a concave grating of 15,000 lines to the inch and a radius of curvature of six feet. The wave-lengths to which they are referred are the most recent values given for the neon lines by Priest, of the Bureau of Standards (Interferometer determinations). In the following table I have given the wave-length differences, the reciprocals of the wave-lengths (frequencies), and the frequency differences. The first six lines (starred) were determined from photographs made with the three-prism spectrograph, as I have not yet obtained a record of them with the grating. The values can be considered correct to two or three tenths of an Ångström unit I think, and represent the position of the centres of the doublets, for the prism spectrograph barely resolved them.

I have used only the first members of the doublets in calculating the wave-length differences, frequencies, &c.

Doublet series excited by green Hg line
(Cooper-Hewitt lamp).

	Dif.	Frequencies.	Freq.-Dif.
7005·5*	91	142850	1880
6909·5*	88·5	144730	1880
6821·0*	88·6	146610	1930
6732·4*	87·4	148540	1950
6645·0* ?	84·3	150490	1930
6560·7*		152420	
6558·4	82·2		1960
Missing			
6396·30		156340	1970
6394·3	79·66		
6316·64		158310	2010
6314·4	79·05		
6237·59		160320	2000
6235·7	76·92		
6160·67		162320	
6158·8			2025
Missing	74·94		
6010·79		166370	2040
6009·1	72·85		
5937·94		168410	2070
5935·0	72·06		
5865·88		170480	2050
5864·8	69·77		
5796·11		172530	2090
5794·6	69·28		
5726·83		174620	2090
5725·3	67·86		
5658·97		176710	2113
5657·4	66·90		
5592·07		178823	2107
5589·8	65·17		
5526·90		180930	2195
5525·2	66·16		
5460·74 (Hg)		183125	2158
5397·13	63·31	185283	
5342·63	59·50		2067
5337·63		187350	

The last two lines form a wide doublet, and are very faint: they appeared on only one plate, and I am not sure about fitting them into the series. I have taken the *second* member in this case in making the calculations, as it fits the series better. The 5397 line is not a doublet, neither can I find any indication that the 5460·7 line (the primary line) is double, though it is accompanied by faint companions like all the other doublets, as we shall see presently. I took great precautions to prevent any diffused light from the mercury arc from getting into the spectroscope, but it is just possible that this line is really emitted by the iodine vapour as a doublet, the gap between the components being filled up by stray light from the arc, which would be the case if the doublet were symmetrical about the green mercury line.

As is apparent from the table, the frequency differences increase a trifle in passing from one end of the spectrum to the other.

The photographs of the entire resonance spectrum taken with the concave grating were made with a very fine slit, and were not fully exposed even with a 24 hour exposure. The lines were beautifully sharp, and served admirably for measurement, but they are scarcely strong enough to bear reproduction. A portion of the spectrum, however, was taken on an isochromatic plate which is much more sensitive in the yellow, and this plate is represented on Plate XVII., F. The lines are rather broad on this plate, and the fainter companions of the doublets come out as well: these will be discussed presently. Spectrum G was made of the vapour excited by the light of the quartz mercury arc, while F was made with the glass Cooper-Hewitt lamp. The resonance spectra will be found to be quite different in some respects. On Plate XVI. will be found the resonance spectra photographed with the large prism spectrograph. All of the spectra, with the exception of A, are reproduced as negatives, as the lines came out better. On this plate A and B are the spectra excited by the Cooper-Hewitt lamp, C by the Westinghouse quartz lamp, D the resonance spectrum excited by the green line acting alone (quartz lamp), and E the spectrum excited by the two yellow lines acting alone. Spectrum D is the series of doublets which we have just discussed, though they are not resolved on the plates which are reproduced.

We will now consider the series excited by the two yellow lines. The more refrangible of the two yellow lines excites a series of doublets when we employ the Cooper-Hewitt arc. These can be seen in spectrum B. If the quartz arc is used (spectrum C) we find triplets in place of the doublets, the middle component being very strong, and the two outer ones weak. This is due to the fact that we have a different distribution of intensity in the mercury exciting lines in the two cases. The wave-lengths given in the following table are determined from plates made with the Cooper-Hewitt lamp. Values starred were from plates made with the prism spectrograph.

Series excited by the two Yellow Mercury Lines.

6547 *	75	6659·2	81·2
6540·2*		6578·0	
6472 *	78·6	6571·7	80·5
6466·4*		6487·5	
6388·4*	82	6481·0	81·5
6384 *		6406·0	
6306·5*	82	6404·2	78·2
6299·5*		6327·8	
6224·53	77·2	6324·6	84·9
6219·84		6342·93	
6147·30	77	6240·24	80
6143		6163·62	
Missing		6153·40	77
5993·28	74·4	6092 *	
5988·21		6086·5*	76·5
5918·90	72·5	6083 *	
5914·02		6010 *	79
5846·36	76·7	5931·24	
5841·29		5865	66·2
5769·60 Hg		5790·66 Hg	74·3

The wave-length differences are not as regular as in the case of the series excited by the green line, and there is no point in calculating the reciprocals or frequencies in this case.

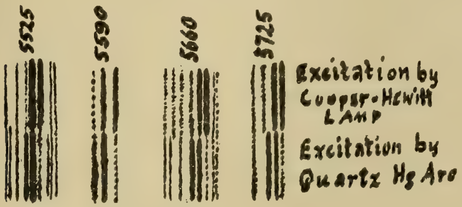
The distances between the components of the doublets excited by the more refrangible of the two yellow lines varies from 4·5 to 7 Ångström units, which in itself indicates that the series spacing cannot be uniform.

The series excited by the yellow line of longer wave-length is still more lawless! Some lines are single, some double, and one triple.

Structure of the Lines under High Resolving Power. Multiplex Excitation.

If we examine under high resolving power the series of doublets excited by the green mercury line, we find a remarkably complicated structure which appears to result from the circumstance that we are dealing with multiplex excitation. The spectra were photographed with a concave grating of six-foot radius, ruled with 15,000 lines to the inch. The iodine tube was excited by the Cooper-Hewitt lamp, and a portion of the photograph obtained in this way will be found reproduced on Plate XVII. spectrum F. This same region excited by the quartz lamp will be found immediately below (spectrum G). It is quite apparent that the component lines which accompany the doublets are quite different in the two cases. Moreover, in the latter photograph it will be found that the doublets are displaced toward the region of shorter wave-length, with respect to those in the spectrum excited by the Cooper-Hewitt lamp. The difference between the two spectra is more clearly brought out by the drawing reproduced in fig. 1, which was very carefully made from

Fig. 1.



photographs obtained with a very fine slit, which are not suitable for reproduction. The component of the doublet which has the longer wave-length in the case of the quartz arc excitation is in coincidence with the component of shorter wave-length in the photograph obtained with the Cooper-Hewitt lamp, in which we find, however, a faint line exactly in coincidence with the other component of the doublet. What is more remarkable, however, is the absence of coincidence in the case of some of the fainter lines. The line at wave-length 5460 is accompanied by fainter companions spaced in much the same way as are the companions accompanying the doublet, but the main line is not itself double.

If we compare the groups at 5460, 5526, and 5658 in spectrum G, we cannot but help being struck by the marked similarity between them, and by the similarity between the arrangement of the lines in the groups and the arrangement of the iodine absorption-lines which occupy the region covered by the green mercury line (spectrum O). The resonance groups are, however, on a vastly larger scale than the iodine absorption-lines, the amplification being about thirty-fold. This is most strikingly brought out in spectra K and L, which represent enlargements of the groups at 5526 and 5658 respectively. The width of the 5461 mercury line, within which all of the absorption-lines which respond to the excitation fall, is shown on the same scale at M. Speaking figuratively, we may say that the iodine vapour acts something like a specro scope of high resolving power, an extremely narrow group of absorption-lines giving rise to similar groups on a much larger scale disposed at regular intervals along the spectrum.

We are now confronted with a great difficulty, for the groups are by no means strictly identical with each other or with the groups of absorption-lines, and we must ascertain if possible which lines in the resonance group are associated with, or excited by, the lines in the absorption group.

I have made a beginning towards the solution of this problem by removing certain frequencies from the green mercury line by passing the light from the arc through bromine vapour before it entered the iodine tube. Some of the bromine lines coincide almost exactly with the iodine lines, and these therefore cannot respond to the excitation, since the necessary frequencies have been removed by the bromine filter. To apply a selective ray-filter within the region of the spectrum occupied by a single emission-line seemed at first a rather large undertaking, but the plan was found perfectly feasible, and very satisfactory photographs were obtained. The circumstance that the satellite lines (if one may so term them) which accompany the resonance doublets are somewhat differently disposed according as we use the green line of the Cooper-Hewitt lamp or the quartz lamp, furnishes us with another method of analysis. Up to the present time I have photographed only the satellite lines grouped around four of the resonance lines; and the circumstance that the general appearance of the groups of lines reminds one of a highly magnified image of the group of absorption-lines falling within the green mercury line, made me think at first that each line in a resonance group resulted from the stimulation of a definite absorption-line. I no longer believe that this is the case, however, and until a further study of the subject is made it will be difficult to say just how the groups arise.

A study of the green mercury line in comparison with the absorption spectrum of iodine in the same region, with the mercury lamp running at different temperatures, throws some light on the subject however, and has most clearly indicated the lines along which the work must be carried in the future.

We are dealing with a group of seven iodine absorption-lines, which for convenience we may designate as two doublets and a triplet, and number 1, 2, 3, 4, 5, 6, and 7, beginning at the short wave-length end (first doublet). If the mercury arc is running at a low temperature, as is the case in the Cooper-Hewitt lamp, the bright central component of the green line almost exactly bisects the second doublet (lines 3 and 4). It is obvious that, under these circumstances, one of the absorption-lines is excited by a frequency slightly greater than its own, and the other by a frequency slightly less. The light which is re-emitted without change of wave-length (resonance radiation) gives us a single line so far as I have been able to find with the comparatively low dispersion brought to bear upon the resonance spectra. The 40-foot spectrograph would probably show it double of course. The lines of the resonance spectrum, however, are double, and the components of each doublet are separated by a distance about 30 times as great as the distance between the absorption-lines. This magnification of the doublet occurs only in the case of the light which is emitted with altered wave-length, and not at the primary line. As a working hypothesis we may ascribe it to excitation by a frequency intermediate between the frequencies of the absorption-lines; and we may test our hypothesis by slightly altering the frequency of the exciting line, so as to make it approach one or the other of the two absorption-lines. It seems by no means impossible to accomplish this, since the distance between the absorption-lines is only $\frac{1}{120}$ of the distance between the D lines of sodium; and a very slight alteration in the pressure of the mercury vapour would give the required shift of the emission-line. If the iodine vapour is excited by the quartz lamp we still get sharply defined lines in the resonance spectrum, notwithstanding the circumstance that, in this case. the green mercury line has broadened out into a continuous band of light, which completely covers the group of absorption-lines with the exception of the point midway between lines 3 and 4, where the green line is weakened by reversal.

This makes it seem doubtful if the hypothesis just suggested is correct. It will be necessary to excite the iodine vapour with the mercury lamp running under several different conditions as to current and temperature before any very definite statement can be made. That this method of investigation is sure to be a very fruitful one is made clear by spectrum N, Plate XVII., on which I have shown the appearance of the green mercury line with the lamp at different temperatures, and the iodine absorption-lines in coincidence with it. This is a drawing. Spectrum O, Plate XVII., is a photograph of the green emission-line of the quartz arc, when first ignited, taken in coincidence with the same line from the lamp at high temperature, the light being passed through iodine vapour. It will be seen that under this condition practically all of the light of the line is located in the strong middle component which bisects absorption-lines 3 and 4. It will be noticed, however, that the centre of gravity of the line lies a little nearer line 3, whereas in the case of the Cooper-Hewitt lamp which operates at a low temperature with about 3 amperes, the green line exactly bisects the absorption-lines, as is shown by the photograph S, Plate XVIII. (upper spectrum the green line, lower spectrum iodine absorption). The green line of the Cooper-Hewitt arc seen "end-on" is shown by spectrum P, Plate XVIII., together with the iodine absorption-lines. In this case the companion lines are enormously intensified in comparison with the middle bright component, which is weakened by self-absorption. The quartz arc, when first started, takes about 8 amperes, and the vapour is undoubtedly denser than in the Cooper-Hewitt lamp. This causes a slight apparent shift of the centre of gravity of the line towards the region of shorter wave-length, due to the brightening of faint components which lie close to the main line on this side. The green line of the quartz lamp at low temperature is shown in coincidence with the same line at high temperature by spectrum Q, Pl. XVIII., and the high temperature line in coincidence with the iodine absorption-lines by spectrum T. Spectrum U shows the line at medium temperature together with the absorption-lines. These photographs were all made with the 40-foot spectrograph in the fourth order. Going back now to diagram N, Plate XVII., we see that the exciting line may be made to assume a variety of intensity distributions according to the temperature and current consumption of the lamp. At medium temperatures we find two dark lines within the broadened emission-line (next to last diagram N). The left-hand one of these I find results from reversal of the central component, and it persists as the temperature rises, as shown by the lower diagram. The right-hand one is the dark gap between the main line and the first component to the right, and this one gradually fades out as the temperature rises.

It is evident that much will be learned when photographs of the resonance spectra are secured with the iodine vapour excited by the line under all of these different conditions. At present we have at our disposal only the resonance spectra excited by the Cooper-Hewitt lamp, and the quartz lamp at high temperature. The change in the appearance of the four groups of resonance lines is shown in fig. 1 (p. 687), which was drawn from the original negatives used for the preparation of spectra F and G, Plate XVII. The most conspicuous feature brought out is that the strong doublets are shifted towards the violet in the case of the excitation by the high temperature arc. It is not an actual shift, but merely a change in the distribution of intensity among the lines forming the groups. In addition to this, certain lines appear in one case which are absent in the other. This is especially noticeable in the group at 5725, in which the second lines from the left are clearly displaced with reference to each other. I am of the opinion that the shift in the region of maximum intensity towards the violet in each group results from the widening of the green line in the same direction; but it seems impossible to assign the lines in the groups to definite absorption-lines until photographs have been secured with the exciting line under a larger number of different conditions. Very probably the excitation of a single line gives rise to resonance lines accompanied by fainter companions. The primary line at 5461 is accompanied by these companions but is itself single, as I have already pointed out. In addition to varying the temperature of the lamp, we may pass its light through bromine or some other vapour showing fine lines in its absorption spectrum, and so modify the appearance of the emission-lines. This has already been accomplished. The light from the quartz arc, rendered convergent by a large condenser, was passed through a large spherical flask containing a small amount of bromine *in vacuo*. The air was exhausted by freezing the bromine to the wall with solid CO_2 and ether, and exhausting rapidly with a Gaede pump. The effect of the bromine filtration was to remove the right-hand component of the triplet which lies to the left of the strong doublets at 5525 and 5660. (See small inserts below spectrum G.) This same triplet is found to the left of the primary line in the resonance spectrum (5461), and the bromine filtration weakened the right-hand member in this case also.

I have photographed the bromine absorption spectrum in coincidence with that of iodine with the 40-foot spectrograph. The two are shown by spectrum V, Plate XVIII., taken with sunlight, and by spectrum R, taken with the green line of the quartz arc. It seems probable that the line removed from each resonance group by the bromine filtration of the exciting light results from one of the absorption-lines 2, 6, or 7, since these three are in coincidence with bromine absorption-lines. We find, however, that the two outer components of the triplet appear in the resonance groups excited by the Cooper-Hewitt lamp, which has practically no energy at the point occupied by the iodine absorption-line 2, while line 7 of the iodine absorption is in coincidence with the right-hand component of the mercury line (see P, Pl. XVIII.), I imagine therefore that this line is responsible for the right-hand member of the triplet removed by preliminary filtration of the green line through bromine. Further experimentation will of course be necessary before we can be at all sure of this point; and I have attempted an analysis merely to indicate the line along which work is possible. The effect of the bromine filter is shown by the small photographs of groups 5525 and 5660 attached to spectrum G.

Transformation of the Resonance into the Band Spectrum by Gases of the Helium Group.

A further study of the remarkable transformation of the resonance spectrum into the band spectrum, which occurs when the iodine vapour is in helium at a pressure of a few millimetres, has been made, and some photographs superior to those published with my first paper have been secured. These are shown on Plate XVII. Spectrum H is a portion of the resonance spectrum between the green mercury line (to the left) and the two yellow lines (to the right), the iodine being in a high vacuum. Spectrum I shows the effect of introducing helium at 2 millimetres pressure, and spectrum J the effect of helium at 10 millimetres pressure. The other gases of the helium group behave in the same way, and I have recently found that the band spectrum can be brought out by the presence of air at one or two millimetres, though the intensity of the fluorescence is enormously weakened, and long exposures are required. It is my plan to investigate this side of the subject during the coming winter. One of my tubes which originally was highly exhausted, and showed only the resonance spectrum, after long use showed traces of the band spectrum. I have therefore prepared some tubes containing only iodine vapour, that is no solid crystals, to see whether prolonged illumination eventually destroys the vapour. It is of course a very delicate matter to speculate about the result of any such experiments, and sufficient data are not yet at hand to make their discussion worth while.

Destruction of the Fluorescence by Temperature.

It will be remembered that I found that the fluorescence of mercury vapour is destroyed by raising the temperature of the quartz flask with a blast-lamp. The same thing is true of iodine, which however loses its luminosity at a temperature so low that the effect can be shown with a tube of soft glass heated with a small Bunsen flame.

There is an immense amount of work to be done with iodine; and if we are ever to learn anything about these enormously complicated absorption spectra, it is my belief that the subject must be attacked along the lines indicated in this paper. This recent work puts a new light on some of the results found with sodium vapour, which can now be repeated to advantage. In every case it will be essential to study the exciting line in connexion with the absorption spectrum at the same point with a resolving power in the neighbourhood of 300,000. In continuing the work I propose to have the exciting line under observation with an echelon or large grating throughout the exposure. An attempt will also be made to operate the mercury arc in a magnetic field.

I have been aided in this investigation by a grant from the Rumford Fund of the American Academy of Arts and Sciences.

LXVII. *On the Deduction of Thermodynamical Relations.*

By Dr. R. A. Houstoun, *University of Glasgow* [*].

IN a recent paper[†] with the above title Prof. J. P. Kuenen criticises the proofs of certain theorems of mine [‡], which appeared in this journal. He finds that my results are valid but arrives at them by another method.

His criticism of the proof of my relation between torsion and tension is owing to a misunderstanding due to the condensed way in which the proof was given. I was considering adiabatic changes although I was aware the relation held also for isothermal changes.

In the other point raised, *i. e.* the proof on p. 82 of the paper on magnetization, I am at fault in not noticing that that proof holds for an adiabatic process while the earlier one is for an isothermal process.

With reference to the main purpose of Prof. Kuenen's paper, I doubt the superiority of his methods. I admit that they are shorter and more elegant, but it is not at all so easy to get a grasp of the physical ideas behind them. And that, I think, is the real reason they have not proved popular. For, of course, they are not new.

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[*] Communicated by the Author.

[†] Phil. Mag. [6] xxiii. p. 752 (1912).

[‡] Phil. Mag. [6] xxi. p. 78 (1911); xxii. p. 740 (1911).

LXVIII. *The Radioactivity of Terrestrial Surface Materials.*

By J. Joly, *F.R.S.*[*]

A SOMEWHAT considerable experience of the electric furnace as a means of determining the radium content of rocks[†] has led me to the conclusion that a revision of the subject of terrestrial radioactivity by its means is desirable. This view is founded upon two circumstances: (1) the method by fusion possesses features rendering it more reliable than any other method, and (2) in its results it differs considerably from the method by solution.

As regards the first point, the reliability and searching character of the method, I have dealt with the subject elsewhere (*loc. cit.*). It may, however, be well to recall here that in this method the emanation is taken directly from the pulverized rock while this is being decomposed by the alkaline carbonates at temperatures rising to 1100° C. or more. In this process the melt possesses but small bulk and the exposed surface is very large. In fact the melt makes but a shallow film in the platinum boat in which it is being heated. (I refer now to the use of the tube furnace.) There is complete decomposition and intense ebullition lasting for about half an hour. The gases evolved are led through a soda-lime tube; the unabsorbed gas (for the most part air driven by thermal expansion from the furnace) is stored in a strong rubber bag, and finally carried again through the soda-lime tube into the electroscope; a final current of air washes out both furnace and tube, and ensures that practically the whole of the emanation is brought into the electroscope. The completeness of the wash-out has been tested by filling a second electroscope through the entire system: when little, if any, residual emanation has been detected. It may, therefore, be assumed that, sensibly, all the emanation evolved in the furnace reaches the electroscope. There is no reason to assume that any part of it leaks through the platinum. Such an occurrence, in view of the high atomic weight of emanation, would be contrary to expectation: moreover, tests carried out on varying quantities of material have been quite satisfactory.

Hardly less important is the protection against contamination, which naturally arises in the simple nature of the procedure involved. The rock is pulverized till it passes a sieve of about 25 mesh to the centimetre. From seven to ten grams are weighed out and mixed with the alkaline carbonates or other fluxes required. The mixture is put directly into the furnace. The platinum boat and all parts of the furnace may be completely de-emanated by a preliminary heating, if thought requisite. When experiments are being made daily this naturally comes about. All the risky chemical operations of the method by solution—often involving a succession of filtrations and fusions—are here avoided.

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[*] Communicated by the Author.

[†] Joly, Phil. Mag. July 1911.

But the most important advantage which can be claimed for the method by fusion has still to be mentioned. The method by solution is exposed to a source of error in the liability of the radium present to assume the non-emanating form—by adsorption or precipitation or from some other cause. This is now fully recognized. It may be sometimes detected in the erratic nature of results obtained in successive experiments upon the one solution. Sometimes it appears as if the presence of sulphates or gelatinous silica was requisite. It is matter of satisfaction that Messrs. Eve and McIntosh, who first drew attention to this in the present connexion, are now investigating the subject[*]. It does not appear probable that any risk of this kind can beset the method by fusion.

The second point to which I referred above—the fact that there is a substantial difference in the results of experiments made by solution and by fusion—will be illustrated in the data contained in this paper. A study of the published results obtained by solution shows much divergency. It seems certain that this largely arises in the actual nature of the material. But the means of several observers are very different. They appear to leave in uncertainty some of the most general questions arising : *e. g.*, the true mean for acid, intermediate and basic rocks and the difference between the radium content of primary and secondary rocks[†].

In this paper—which is preliminary in its scope—I shall deal with general results rather than with details. Thus the question of "magmatic differentiation" as an influence in the segregation of radium I have put aside for the present ; on that account leaving out determinations upon differentiation products or what are believed to be such. The acid, intermediate, and basic magmas, as represented by undifferentiated plutonic, injected, or volcanic materials, are alone dealt with, because these are primarily involved in the wider geological applications of radioactivity.

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[*] *Vide* Eve and McIntosh, Phil. Mag. Aug. 1907, and Trans. Royal Society of Canada, 3rd series, 1910, p. 67.

[†] A recent investigator has actually questioned if there is any such difference, and points out that certain solution results on trachytes are actually lower than his own results on limestones. Büchner, *Konink. Akad. van Wetenschappen te Amsterdam*, Jan. 1911.

The method pursued is different from what has hitherto been adopted in such investigations. Individual rock specimens are not dealt with. A large number of typical rock samples are reduced to powder. A similar weight of each is taken and the added powders thoroughly mixed. The determination in the furnace is made upon one or more samples of this composite powder. If there is anything to suggest abnormality in the result, a second determination is made upon a composite powder compounded of about one half the original samples. If a high result was due to the presence of *one* very radioactive rock, this fact must be detected in this second experiment. If it is desired to eliminate such an excessively radioactive material it may be rapidly isolated by a few successive experiments upon one half, one quarter, &c. of the original samples separately compounded. This method has many advantages. At this stage of the inquiry it yields all the information required. The labour does not increase with the number of rock specimens; on the contrary, the more rocks enter into the composite material the less need to consider individual abnormalities, or, we might say, the more the necessity for their inclusion. As the number of available rock specimens increases I hope to place the means arrived at in this manner upon a more secure basis.

There is a certain small latitude of uncertainty in the results. The "constant" of furnace and electroscope working in conjunction, as determined by dealing with known amounts of radium, may vary somewhat. In a series of experiments carried out to ascertain the constant proper to the present series of experiments, variations of its value from 0·7 to 0·8 were obtained. The mean of these values has been taken. Comparison with results obtained when this method was first being developed (*loc. cit.*) will show that this value is well supported by other observations. In experiments upon the sedimentary rocks, carried out in my laboratory, a somewhat lower constant, *i. e.* 0·6, was arrived at*. The difference is probably due to the electroscopes used in the two cases. It is satisfactory that the results on composites of the sedimentary rocks, given further on, wherein the higher constant is used, almost exactly substantiate means arrived at on the detailed results calculated on the lower constant. This not only brings the latter measurements into line with those on the igneous rocks, but it supports the value of the constant assumed above.

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* Fletcher, Phil. Mag. Feb. 1912.

In the following table of results the quantities of radium are, as usual, expressed in billionths of a gram per gram of rock, and must, therefore, be multiplied by 10^{-12}.

IGNEOUS ROCKS.

Acid.

63 Granites	2·7	Mean 3·01 for 86 rocks.
23 Intrusive and volcanic	3·9	

Intermediate.

12 Syenites	2·4	Mean 2·57 for 48 rocks.
8 Diorites	1·6	
18 Trachytes	3·0	
10 "Porphyries"	2·8	

Basic.

5 Gabbros and Norites	1·3	Mean 1·28 for 31 rocks.
8 Diabases and Dolerites	1·0	
14 Basalts and Melaphyres chiefly Deccan and Antarctic	2·0	
11 Basalts chiefly Hebridean	0·5	
18 Basalts generally representative	1·4	

Additional.

7 Vesuvian lavas	12·6
14 Gneisses, various	2·1

In selecting rocks for the foregoing determinations I have endeavoured to include material as representative as possible. In the composites of the intrusive and volcanic series, differentiation products are excluded ; *i. e.* the chemical extremes of the groups. But it would seem from the results as if differentiation had operated to segregate radium in these rocks. The interesting question is raised as to how far such differentiation is indicative of more general effects of the kind, or may serve to indicate general differentiation. I hope to return to this question at a later date, when composites of the complementary differentiation products are being examined.

The three composites of basalts serve to illustrate the divergence which exists in the radium content of these rocks. Thus the fourteen rocks, of which one only is from the great Hebridean outflow and ten are from the Antarctic and Deccan areas, possess four times as much radium as the Hebridean basalt. The result for the latter confirms Strutt's low figure for this rock *. Finally, a carefully made up composite, in which basalts from the most widely separated areas are equally represented, gives a value approximating to a mean between the high and low results. The general mean for basic rocks includes the more representative series of basalts only. Of the Additional rocks, the gneisses not being in all cases of certain igneous derivation, are not available for general deductions.

For comparison with the determinations by fusion I have classified below the results obtained in some of the leading investigations in which the method by solution has been employed. The numbers in brackets given after the results indicate the number of rocks dealt with.

	Granites.	Acid Intrusives and Volcanics.	Syenites.	Diorites.	Trachytes and Andesites.	Gabbros and Norites.	Dolerites and Diabases.	Basalts.
Strutt [1]	2·74 (10)	1·03 (1)	2·67 (3)	0·99 (1)	...	0·63 (1)	0·59 (2)	0·44 (8)
Farr & Florance [2]	1·75 (2)	1·90 (1)	...	...	1·68 (4)	0·33 (2)	0·59 (3)	0·81 (1)
Schlundt & Moore [3]	...	1·95 (7)						
Büchner [4] ...	3·70 (5)	0·80 (3)	...	0·80 (3)	1·85 (12)	0·70 (1)	0·87 (2)	0·50 (1)
Fletcher [5] ...	0·85 (4)	...	...	...	0·85 (20)	...	...	0·71 (5)
Mean	2·51 (21)	1·58 (12)	2·67 (3)	0·85 (4)	1·21 (36)	0·50 (4)	0·67 (7)	0·56 (15)

[1] Strutt, Proc. R. S. lxxvii. A. p. 472, and Proc. R. S. lxxxiv. A. p. 377.

[2] Farr & Florance, Phil. Mag. Nov. 1909.

[3] Schlundt & Moore, Bull. U.S. Geol. Survey, p. 395 (1909).

[4] Büchner, Konink. *Akad. van Wetensch. te Amsterdam,* Proc. Oct. 1910, and April 1912.

[5] Fletcher, Phil. Mag. July 1910; Jan. 1911; June 1911. In the analysis given above the series of observations on the Leinster granite are treated as representing but one rock. Otherwise a considerable lowering of the mean for granite must arise. I have not dealt similarly with the series on the Andine lavas, as these appear to include distinct outflows and petrologically distinct varieties of trachytes and andesites.

When the means for acid, intermediate, and basic rocks are calculated from the above table, giving equal weight to each separate rock determination, we have:—

Acid,	mean for 33 rocks	2·17
Intermediate,	,, ,, 43 ,,	1·28
Basic,	,, ,, 26 ,,	0·58

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* Strutt, Proc. R. S. lxxxiv. A. p. 377.

It will be seen that these depart considerably from the means obtained on composite rock-powders, using the method by fusion; the intermediate and basic groups, more especially, are about 100 per cent. of their value too low if the method by fusion gives correct results.

I have in the above analyses of results by solution omitted some results of my own [*] which afforded generally higher values than those obtained by other investigators using the same method. No clue to this difference is as yet forthcoming, and until the results by fusion were obtained it seemed best to assume that some difference in the preparation of the solutions was responsible, in which case the higher results would be the more reliable. However, many of my determinations by solution stand some fifty per cent. (or even more) of their value above the fusion results, and as it seems improbable that emanation can be retained when the latter method is employed, it seems safer to set aside for the present such determinations of mine as have not been confirmed by the use of the electric furnace. A remarkable fact is that just some of the highest of my results have been so confirmed. Thus, in the results obtained by composite fusions given above, the mixed powders of seven Vesuvian lavas give 12·6. The results obtained by solution on these same lavas would afford a mean value of 10·8 [†]. Again, eleven of the St. Gothard granites gave 7·2 by solution, and six other examples of this granite gave by fusion 6·0 [‡]. I have also omitted some high values obtained by Gockel using the solution method [§]. These results give a mean of 74·6 for six rocks. His low results are obtained by a radiation method, and are not easily compared with the measurements by solution.

In his first paper (*loc. cit.*) on the subject of terrestrial radioactivity, Strutt pointed out that the acid rocks appeared to contain a larger amount of radium than the basic rocks. The fusion results support this conclusion. There are extremes of radioactivity found in all the chemical groups. These may be regarded as exceptional, or set off one against the other. We see such extremes in the basic Vesuvian lavas and in the granites of the St. Gothard or of Karangan [||]. The fact remains that the great body of acid rocks are the richest in radium, and are over twice as rich as the typically basic group. I have shown that the thorium content of the acid rocks is also in excess of that of the basic rocks [*]. No explanation of this is forthcoming. It may arise in the primary differentiation of a parent magma into granitoid and gabbroid divisions. It has been maintained that these divisions represent in themselves fundamental magmas, and that they are present in about equal proportions in the lithosphere [†].

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[*] Address Section C, British Assoc. 1908, and 'Radioactivity and Geology,' Constable & Co.

[†] Joly, Phil. Mag. Oct. 1909.

[‡] Joly, Phil. Mag. Feb. 1912.

[§] Gockel, *Jahrbuch der Rad. u. Elekt.* B. vii. p. 487.

[||] Büchner, *loc. cit.* April 1912.

The connexion between radioactivity and silica content may turn out to be closer than a rough proportionality. If we take the three chemical rock-divisions as characterized by 74, 60, and 48 per cent. of silica and assign to the most acid division a radium content of 3, we find the radium in the other groups, if proportional to the silica, would be 2·4 and 1·9. The basic division departs most from the proportionality, but considering the extreme variations both in silica content and radium content which obtain in this division, the agreement seems sufficiently close to suggest some connexion between the segregation of uranium and of silica in the history of the magma. A similar proportionality is indicated in the thorium content [‡]: but here the number of observations is insufficient. I hope to be shortly in a position to enter more fully into this question.

Coming now to the availability for geological discussion of such results as the foregoing, we are met by the difficulty that we really do not know the quantitative distribution of the several rock families in the lithosphere. When, therefore, we seek to derive a general mean radium content our conclusion may be attended with a certain amount of error. On the result of a very considerable number of analyses of igneous rocks, Clarke [§] concludes that the lithosphere to a depth of ten miles probably approximates in composition to that of a diorite or andesite; or is, in short, "intermediate" in chemical character. If this is correct we should assign to it such a radium content as we find in intermediate rocks, *i. e.* 2·57. If we combine the gabbros and granites we get a mean of 2·0, and if basic and acidic generally are combined the average is 2·2. It would appear as if the radium content of average igneous rocks at the surface is not below 2·0, and may probably be about 2·5. If the entire number of 165 rocks entering into the fusion results are taken, the general mean is 2·60. Any one of these means is considerably in excess of what is deducible from the results obtained by solution.

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[*] *Cong. Internat. de Rad. et d'Elect.* 1911, p. 370.

[†] Loewinson-Lessing, Geol. Mag. 1911, p. 248.

[‡] Joly, *loc. cit.*

[§] 'Data of Geochemistry,' 2nd ed. 1911, p. 26.

When the presence of thorium is taken into account we have the data for a complete evaluation of the number of calories developed per unit of time in average surface rock. The general average for the thorium content of igneous rocks appears to be about $2·60 \times 10^{-5}$ gram per gram [*]. If we take 2×10^{-5} for purposes of calculation, we find $13·28 \times 10^{-14}$ calorie as the heat developed per second per gram. Taking the radium as 2×10^{-12}, we have to add $12·00 \times 10^{-14}$ calorie. The total is 25×10^{-14} gram-degree of heat per second. A material of this degree of radioactivity can only be supposed to extend downwards a relatively small distance. Assuming the surface gradient to be 1° in 35 metres, the conductivity to be 0·004, and the specific gravity of the rock to be 2·7, we find that a downward extension of 17 kilometres (10·6 miles) suffices to account for all the heat reaching the surface.

This conclusion lands us in the difficulty of accounting for the high temperatures which are believed to extensively prevail deep in the crust. At the base of the 17 kilometre layer the temperature due to radioactivity would be no more than 246° C. We are from this driven to the conclusion that rocks of this degree of radioactivity do not, in point of fact, extend downwards till all the radioactive materials present are exhausted. The low radioactivity of certain of the basalts probably affords an indication of the vertical distribution of rocks in the earth's crust. It seems a probable conclusion that such basic and feebly radioactive materials make up the deeper parts of the surface crust, and by carrying the heat-producing elements to a sufficient depth, account for such temperatures prevailing beneath as many geological phenomena seem to require. Thus it will be found on calculation that if basalts with a radium content of $0·5 \times 10^{-12}$ and a thorium content of $1·0 \times 10^{-5}$ carried most of the radioactive materials, temperatures of between 500° C. and 600° C. would exist at depths of some 40 kilometres (25 miles) from the surface [†]. It must be remembered, however, that the thermal state in the depths of the crust is largely matter of surmise. Most indications of deep-seated high temperatures are restricted to the geosynclines and over these sediment-laden areas the surface crust cannot be considered normal.

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[*] Joly, *Cong. Internat. de Radiologie et d'Electricité*, 1911, p. 376.

[†] In a recent determination Mr. Louis Smyth finds the thorium content of the typical composite basalt to be $0·47 \times 10^{-5}$ gram per gram. This result would involve a greater extension downwards and higher basal temperatures than those cited above.

The Secondary Rocks.

The radium content of the secondary rocks has been dealt with by A. L. Fletcher[*], using the method by fusion as it is applied in my laboratory. The results are :—

For 24 arenaceous rocks	1·5
,, 9 altered ditto	1·5
,, 16 argillaceous rocks	1·3
,, 9 schistose ,,	1·1
,, 24 calcareous ,,	0·8

These rocks were treated in detail, the figures are the mean of the several observations in each group. The fact that the argillaceous rocks are inferior in radium content to the arenaceous is to be explained in the nature of the arenaceous materials dealt with. Many of these were by no means ultimate products of solvent denudation, that is were not purely quartzose. The importance of verifying the means for the two leading groups led me to treat composite sediments in the electric furnace. The agreement with the means given above is satisfactory:—

For 39 sandstones, conglomerates, and coarse grits	1·5
,, 20 slates and shales	1·5

It would appear from the comparison of the above with the few published results on sedimentary rocks obtained by the solution method that most of the latter are too low by about 50 per cent. of their value. The leading data known to me are :—

Strutt[†] on 8 slates, sandstones, and clays	1·2
,, on 8 calcareous rocks	1·0
Eve & McIntosh[‡] on 5 clays and limestones	0·59
,, ,, on 8 limestones, sands, & clays	1·02
Farr & Florance[§] on 2 calcareous rocks	0·37
Büchner[‖] on 11 calcareous rocks	1·4

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[*] Phil. Mag. Feb. 1912.

[†] Strutt, Proc. R. S. lxxviii. A. p. 150.

[‡] Eve & McIntosh, Phil. Mag. Aug. 1907; and Trans. R. S. Canada, 3rd ser. 1910, vol. iv. p. 69.

[§] Farr & Florance, Phil. Mag. Nov. 1909.

[‖] Büchner, *Konink. Akad. van Wetensch. te Amsterdam*, Proc. Feb. 1911.

It must be remembered that the calcareous rocks are relatively of little importance in estimating the average radioactivity of the sediments. Estimates of their relative abundance concur in representing them as constituting but a few per cent. (less than 10) of the total sedimentary mass. We infer from this that 1·5 may be accepted as the average radium content of the sedimentary rocks. Results on the amount of thorium in the sediments show that they contain about $1{\cdot}16 \times 10^{-5}$ gram per gram*. From these data we get for the rate of development of radioactive heat in these rocks :—

For the radium 9×10^{-14} cal. per sec. per gram.
,, thorium $7{\cdot}6 \times 10^{-14}$,, ,, ,,

giving a total of $16{\cdot}6 \times 10^{-14}$ cal. The corresponding value for the igneous rocks is, as we have seen, 25×10^{-14} cal.

It is only in the geosynclines, wherein the great body of the sediments has collected throughout vast periods of geological time, that the geological importance of the radioactive heat of the sediments becomes conspicuous. The sedimentary deposits may amount to more than 10 kilometres in thickness. These great masses are laid down upon the normal igneous crust, and the intensification of the deep-seated temperatures thereby brought about would appear adequate to account for the leading facts of mountain elevation. The matter has been dealt with elsewhere†.

The results obtained by the fusion and decomposition of rocks in the electric furnace assign to the sediments 1·5 and to the igneous rocks 2·5 as mean radium content. *Of the existence of a substantial difference between these two classes of materials there appears to be no doubt.*

The denudative loss of radium (which, of course, stands for a measure of the parent substance, uranium) to the ocean is greater than appears at first sight from the foregoing figures; for there is a reduction of mass attending the processes of denudation amounting to about 33 per cent. of the original rock. Hence in the sediments we have but 67 per cent. of the primary rock, and this containing but 60 per cent. of the original radium content. The total loss has been about 60 per cent. of the radium of the primary rock ; or for every tonne of igneous rock converted to sediment the loss of radium has been 15×10^{-7} gram. This is carried into the ocean and remains in its waters and its underlying deposits.

* Joly, Phil. Mag. July & Aug. 1910.

† Joly, Address Section C, Brit. Assoc. 1908.

I have shown elsewhere that it is possible to use the amount of sodium in the ocean as a measure of the total quantity of primary rock which has been denuded in the course of geological history*; and later I calculated by its means the total mass of the sub-oceanic sediments†. These estimates are independent of the duration of geological time. They, in fact, do not involve the *rate* of denudation, but only the integral of its products. The security they possess may be judged from the fact that the only assumption involved in their derivation is that the sodium of the ocean is a product of solvent denudation which has been contributed to the ocean and which, practically, in its entirety now remains to our observation. The rest of the argument is based on our knowledge of the sodium content of average igneous and sedimentary rocks.

The mass of igneous rock, parent to the sediments, proves to be $84{\cdot}3 \times 10^{16}$ tonnes. The radium brought into the ocean has, therefore, been $84{\cdot}3 \times 10^{16} \times 15 \times 10^{-7}$ or 1264×10^{9} grams. This amount must be contained in its waters and in the sub-oceanic sediments. We may first make a deduction for the amount now in solution. Estimates of oceanic radium vary. If we take 4×10^{-12} gram per kilogram or 4×10^{-9} per tonne, we have, multiplying by the mass of the ocean, *i. e.* by $1{\cdot}32 \times 10^{18}$ tonnes, the quantity $5{\cdot}3 \times 10^{9}$ grams as the total amount in solution. The deduction is trifling and leaves 1259×10^{9} grams assignable to the sub-oceanic sediments.

The mass of these in the aggregate is $19{\cdot}5 \times 10^{16}$ tonnes, and hence we must ascribe to them an average radium content of $6{\cdot}4 \times 10^{-12}$ gram per gram.

The following measurements of the radium content of oceanic deposits have been made by the fusion method‡:—

Four samples of Globigerina ooze from depths of 1990 to 2493 fthms.	3·3
Three of the above four samples	3·1
A sample of blue mud, depth 1240 fthms.	1·5
,, "ooze" ,, 720 ,,	1·7
Two samples of Radiolarian ooze from depths of 2600 and 2750 fthms.	13·1
A sample of red clay, depth 2350 fthms.	11·0

From these figures we see that the quantity of radium assignable to the oceanic deposits is in fair agreement with the measurements of the radium content of these materials. This result generally confirms the statistics of solvent denudation. But in a subsequent paper I hope to show that a full consideration of the data now at our disposal respecting the sub-oceanic sediments leads to the conclusion that the less radioactive deposits have been subject to considerable changes in chemical composition during recent geological times, and do not possess throughout their entire mass the chemical composition we observe in samples dredged from their surface. The subject is of sufficient interest to merit separate treatment.

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* Joly, Trans. R. D. S. vol. vii. 2nd ser., 1899.

† 'Radioactivity and Geology,' pp. 57–58.

‡ They are considerably lower than the results which I formerly obtained by solution, but must be considered more reliable.

I desire to thank Mr. Louis B. Smyth and Mr. A. L. Fletcher for some experiments made in connexion with this paper.

Iveagh Geological Laboratory,
Trinity College, Dublin.
Sept. 1912.

LXIX. *Notices respecting New Books.*

Physical Optics. By R. W. Wood, LL.D., Professor of Experimental Physics in the Johns Hopkins University. New and Revised Edition. Pp. xvi + 705. The MacMillan Company, 1911. Price 22*s*. net.

THIS is a new edition of a notable book. It is not an ordinary textbook—it is too full of original matter to serve the purposes of such a manual, and yet it does in some respects endeavour to meet the requirements of the routine studies which every physical student must undertake in order to ground himself well in his subject. Its chief characteristic is that it brings together the large amount of experimental work of a kind for which Professor Wood has a very happy knack, especially in connexion with the subjects of optical dispersion and absorption.

The weakest part of the book is probably that dealing with polarization, especially the chapter on double refraction. Although even here the author brings his characteristics into full play, he is not happy in dealing with the various ellipsoids which are made use of in this part of the subject. For example, the account on p. 310 of the derivation of the ellipsoid of elasticity is either incorrect or it is so obscure that the intended information is not given; the former alternative is probably the correct one. Again, no clear distinction is drawn between ray-velocity and wave-velocity. In connexion with the change of dispersion of the optic axes with temperature it is asserted that "a further elevation of temperature causes the axes to cross one another, so to speak, the crystal becoming again biaxal." No student would surmise from this description that the new plane of the optic axes is at right angles to the plane at the lower temperatures. A short account of the dependence of this change upon the refractive indices would have been welcome and instructive: instead of this, the phenomenon is given merely as "a remarkable phenomenon." Instead of describing the section of selenite used for the experiment as "an oblique section," it would be more lucid to describe it as one perpendicular to the first median line. Imperfections of this sort may seem trivial, but in this chapter they occur fairly frequently, and other chapters are not free from them.

The first half of page 133, indicating a supposed dependence of the order of possible interference upon the regularity of the vibrations of the radiating molecules, merely states the antiquated view, as though it were still thought to be correct. The correct view, given by Rayleigh (also independently by Gouy), appears on p. 136; but the whole treatment requires to be modified so as to remove the contradiction.

New chapters have been added on Meteorological Optics, Electro-optics, and the Principle of Relativity; and considerable changes have been made in some of the other chapters, chiefly in the direction of additions to the experimental part, and a removal of somewhat superfluous mathematics.

With regard to the general appearance of the volume, the reviewer cannot forbear from saying that it would be greatly improved if more attention had been paid to some of the diagrams. Many of these are simply rough script sketches, and they detract very much from the general appearance. Some of these, again, are on such a small scale as to be difficult to make out.

The first edition was marred by a very large number of misprints, chiefly of a fairly obvious kind in formulæ; but, even so, very confusing to a student. Many of these have now been removed; but, unfortunately, it must be stated that a number still remain. Attention may be called to the numerical values given for Fresnel's integrals on p. 247. These are quoted in an erroneous form from textbook to textbook. The most important errors are in the value of the cosine integral for $v=2{\cdot}6$ and $v=1{\cdot}8$: the former should be ·3889 instead of ·3389 (Fresnel's value was ·3895); the value for $v=1{\cdot}8$ should be ·3337 instead of ·3363 (Fresnel's value was ·3342). Reference for other corrections to these integrals may be made to D'Ocagne, *Journal de Physique*, 1902, p. 507, and to Wind, *Physikalische Zeitschrift*, No. 18, p. 265.

Crystallography and Practical Crystal Measurement. By A. E. H. Tutton, D.Sc., M.A., F.R.S., A.R.C.Sc. Pp. 946. Numerous illustrations. London: Macmillan & Co., Ltd., 1911. Price 30/- net.

It is not very long since we received a small book dealing with Dr. Tutton's own researches into crystal structure. The present volume is of quite a different scope; indeed, it provides a complete account of the subject in all its aspects. It is a guide to practical work in crystallography; it includes also all the essential theory of the subject not only as regards crystal morphology but also with regard to the physical properties of crystals. It is, of course, to the latter that we must give first place in this review. This may for our purpose be divided into two parts. There is the part in which Dr. Tutton describes the optical properties of crystals especially in relation to polarized light. This part is most excellently done. Dr. Tutton is fully familiar with this part of his subject, and he has not failed to give a very lucid and full account of it. This part, like all the rest of the volume, is very fully illustrated. The illustrations are good, the majority of them being quite new. Many of them are from photographs by Dr. Tutton himself; these have been taken with great skill, and the publishers have reproduced them with great success. The perspective views, on page 595, of a prism refracting light are perhaps not as happily conceived as most. Even if they may suggest the phenomenon better to some readers, it is probable that most would understand better a plane sectional drawing such as is usually given. This part of the book fills some hundreds of pages and is replete with details, that have never been brought together in the same way before, of methods of measuring refractive indices, optic axial angles, and other data of crystals. In another part Dr. Tutton is not quite so happy. This is when he is giving a summary of what may be described as outlying phenomena such as the Zeeman effect. This criticism may be made of Chapter xxxiv; but, as most of this chapter is in small print, it is clear that the author intends it to take only a secondary place; and we will leave it in such a position in this notice. On the crystallographic side Dr. Tutton gives a full account of the characteristics of the various crystals and of the methods of representing them in stereographic projections. This account has not been unnecessarily encumbered with antiquated phraseology; indeed, the author's attempt has been to lighten the subject as much as possible in this respect. It is needless to say that the conception of molecular distance ratios occupies a prominent place.

Dr. Tutton is a practical worker, and without hesitation we say that he has produced a most practical guide to this subject.

LXX. *Intelligence and Miscellaneous Articles.*

NOTE ON THE DIFFUSION OF ALKALI SALT VAPOURS IN FLAMES AND ON THE MEASUREMENT OF THE VELOCITY OF FLAMES.

To the Editors of the Philosophical Magazine.

Gentlemen,—

In a paper published in your July number on "The Diffusion of Alkali Salt Vapours in Flames," Prof. H. A. Wilson communicates experiments undertaken with the object of finding the coefficients of diffusion of these vapours in a Bunsen flame. A small bead of salt on a platinum wire is put in the flame, and the shape of the region surrounding the bead which emits light is measured. From this and the velocity of the flame gases Prof. Wilson calculates the coefficient of diffusion.

I may perhaps mention that the treatment of this question is not quite new. Already seven years ago the possibility of finding the mass of the particles emitting light was the starting-point of such researches on flame diffusion (see P. Lenard, *Annalen der Physik*, vol. xvii. p. 198, 1905). The measurements were first carried out by Mr. O. Jessel, and then continued and improved by the writer together with Dr. J. Laub (published by A. Becker, Heidelberg Acad. of Sciences for 1911). The method used consists in the determination of the distribution of the vapour emitting light by measuring the distribution of the intensity of the light below the bead of salt. From this and the velocity of the flame the coefficient of diffusion has been calculated (*l. c.* p. 17). We believe that this method, described there in detail, has distinct advantages in comparison with Prof. Wilson's method.

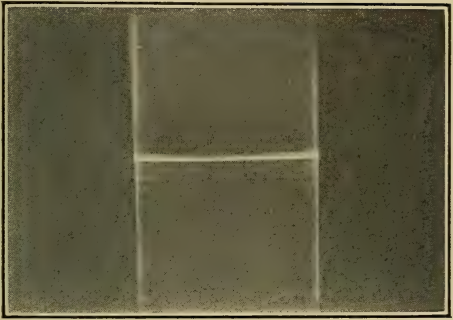
The value of the coefficient of diffusion found by us for sodium is about 1·0, and lies between the values which are to be expected for the atom of sodium and the molecule of its oxide. From this we conclude that the free state of the atom and the chemically combined state of the same atom alternate at about equal intervals. The much higher values found by Prof. Wilson for the coefficients of diffusion seem scarcely well supported by theoretical view. Also Prof. Wilson's conclusions as to the charge of the luminous particles agree so badly with the known results of recent investigations (see P. Lenard, *Annalen der Physik*, vol. ix. p. 642, 1902, and Heidelberg Acad. of Sciences, 1912; E. N. da C. Andrade, Dissertation, Heidelberg, 1911, and Phil. Mag. vol. xxiii. p. 865, & vol. xxiv. p. 15, 1912), that it is hard to believe that they furnish a proof of the correctness of his results. As our researches are being continued, we may return to these points later on.

As to the measurement of the velocity of the flame gases, Prof. Wilson uses a vibrating tuning-fork, and observes the wavy outline of the luminous band coming from a bead attached to one prong of the fork. It may be noticed that this is quite the same method as I have published several years ago (*Annalen der Physik*, vol. xxiv. p. 823, 1907). There are, however, better methods at hand at present. One of these I have given at the same place (*Annal.* vol. xxiv.); it consists in measuring the force exerted on a small ball by the stream of the flame gases (see also A. Becker, *Annalen der Physik*, vol. xxiv. p. 963, 1907, and S. S. Nehru, Dissertation, Heidelberg, 1911). Another method has been published later on by Mr. Andrade (*Annalen der Physik*, vol. xxxvii. p. 380, 1912), who has also made comparisons between the different methods named.

Yours truly,
A. Becker.

Physical Laboratory of the
University, Heidelberg,
July 29, 1912.

FIG. 1.



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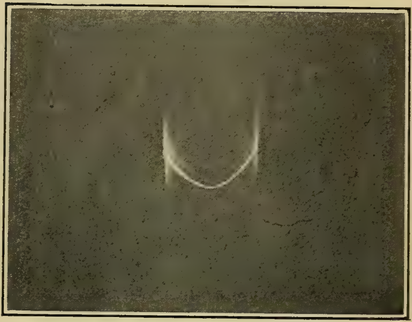

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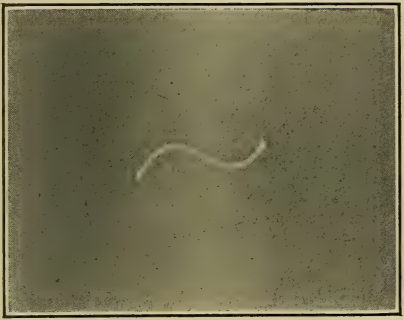

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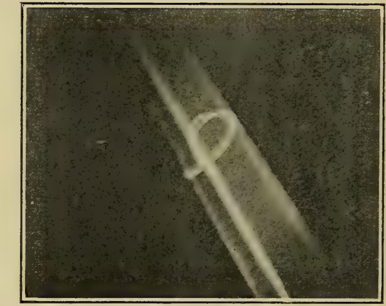

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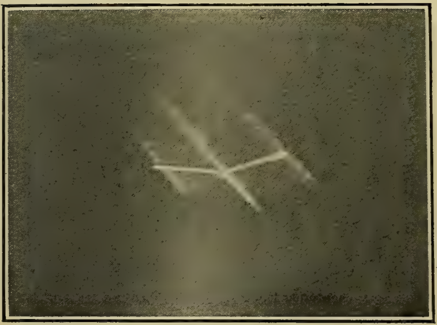

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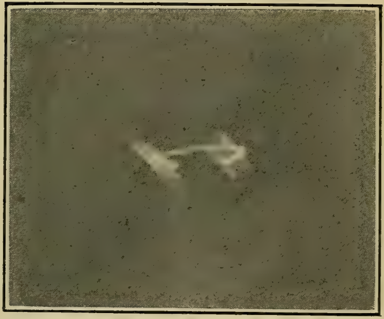

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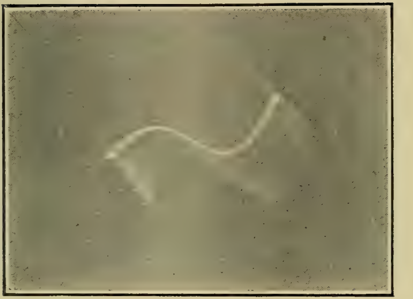

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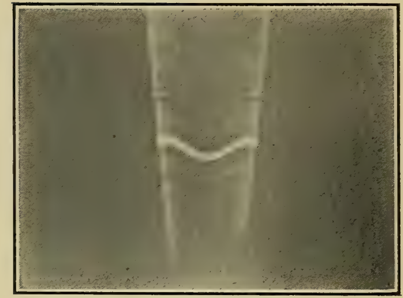

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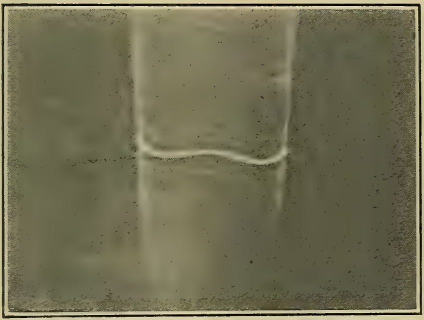

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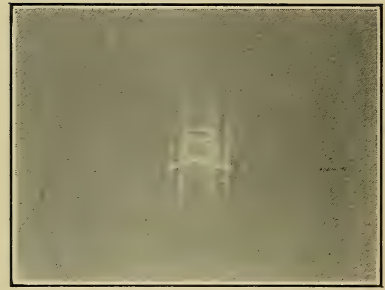

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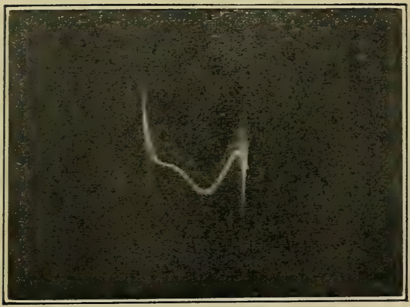

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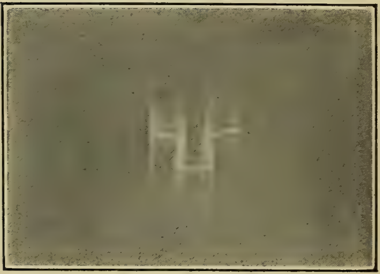

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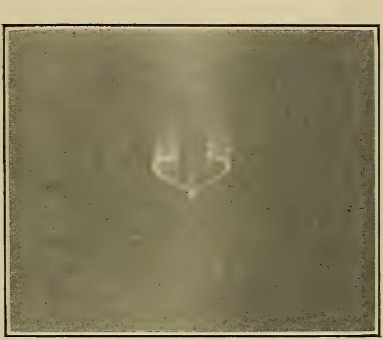

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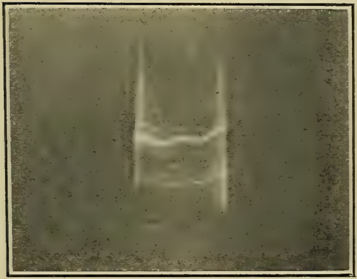

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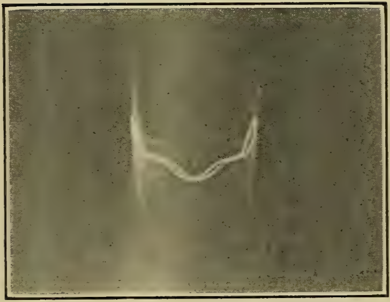

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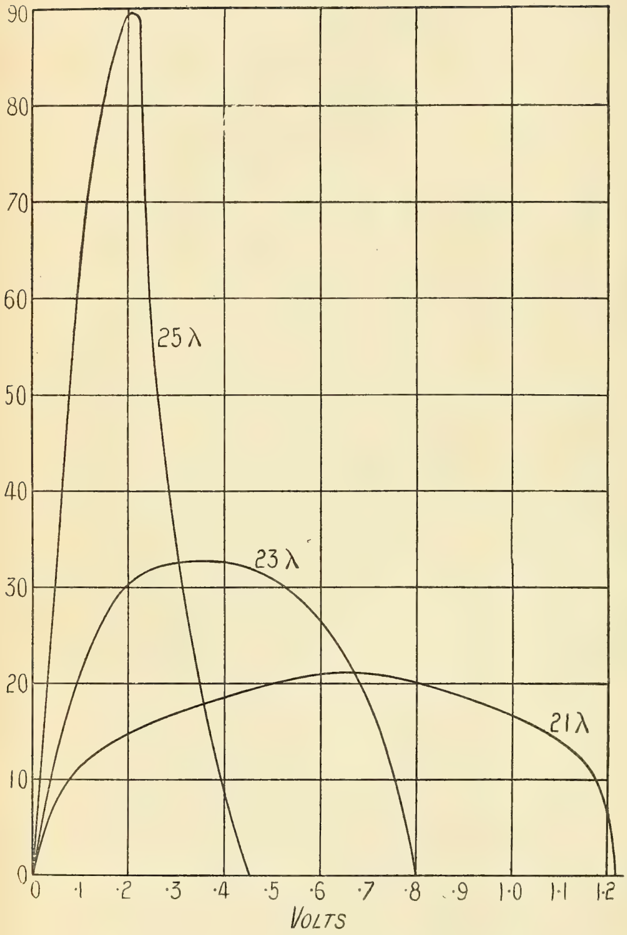
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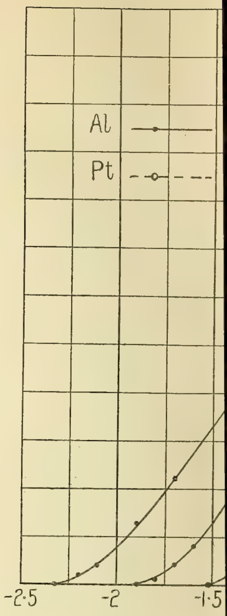
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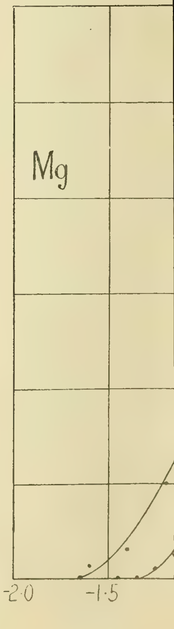
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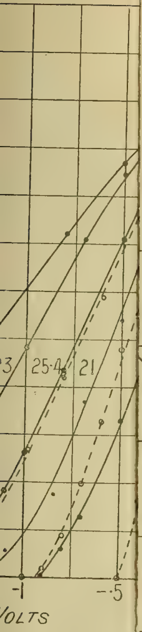

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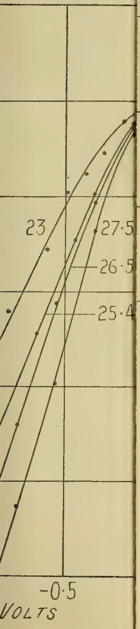

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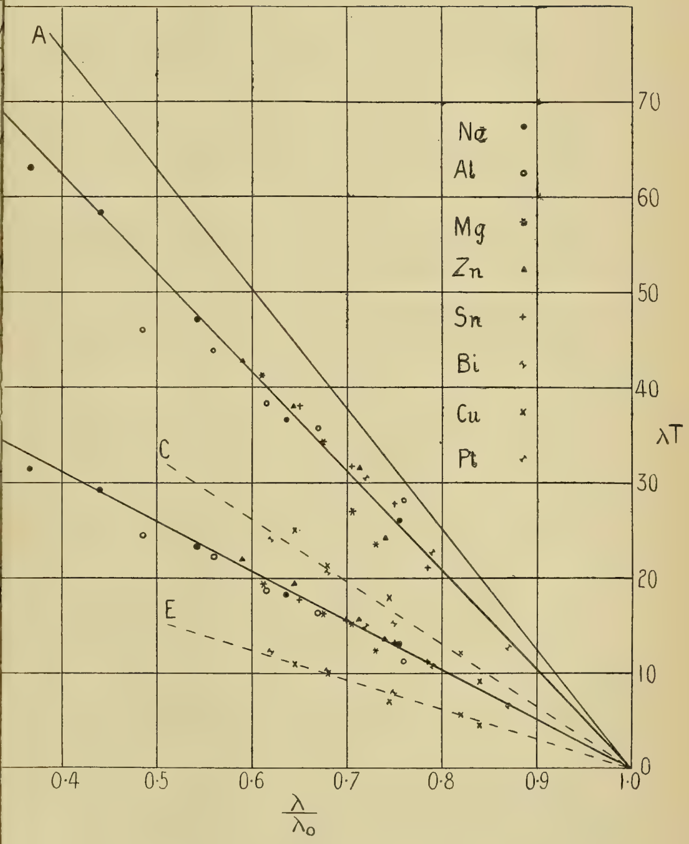
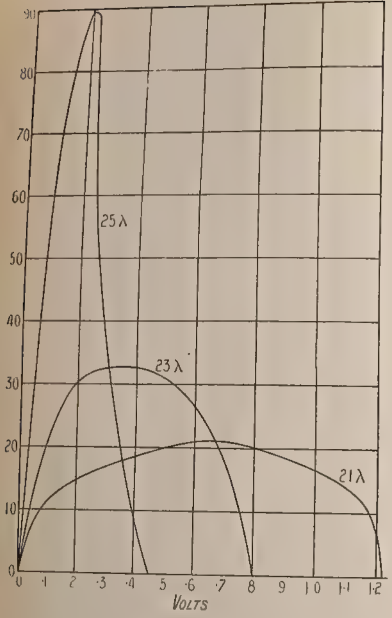


Richardson & Compton.

Phil. Mag. Ser. 6, Vol. 24, Pl. XIII.

Fig. 3.



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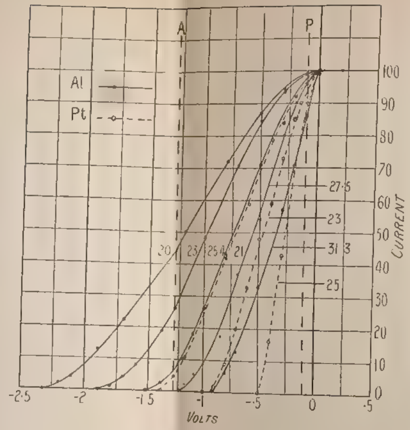

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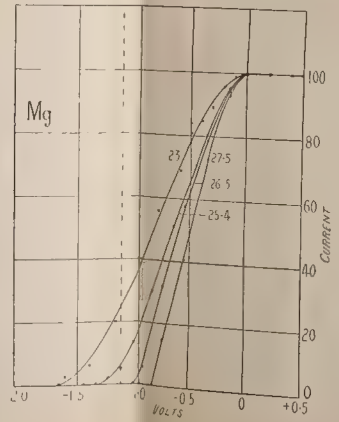

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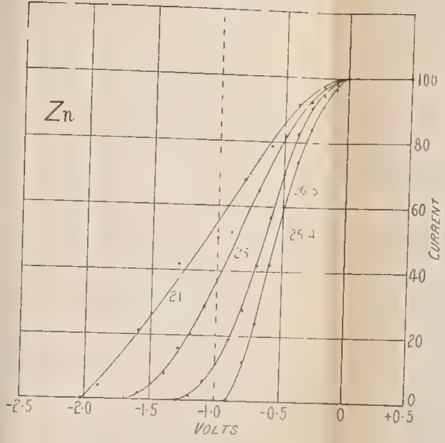

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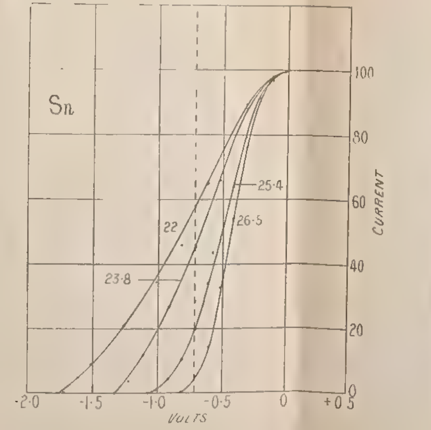

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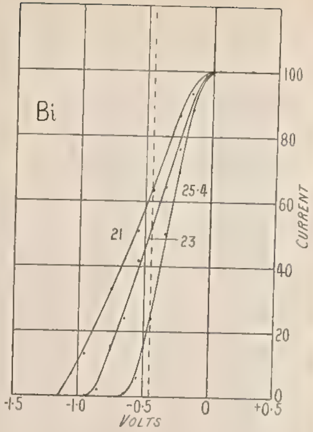

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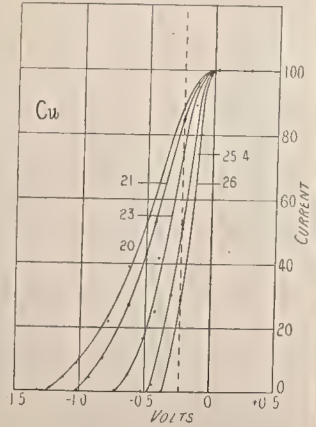

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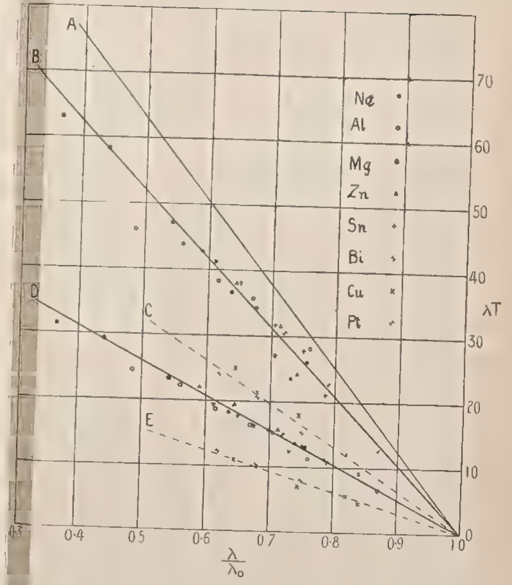

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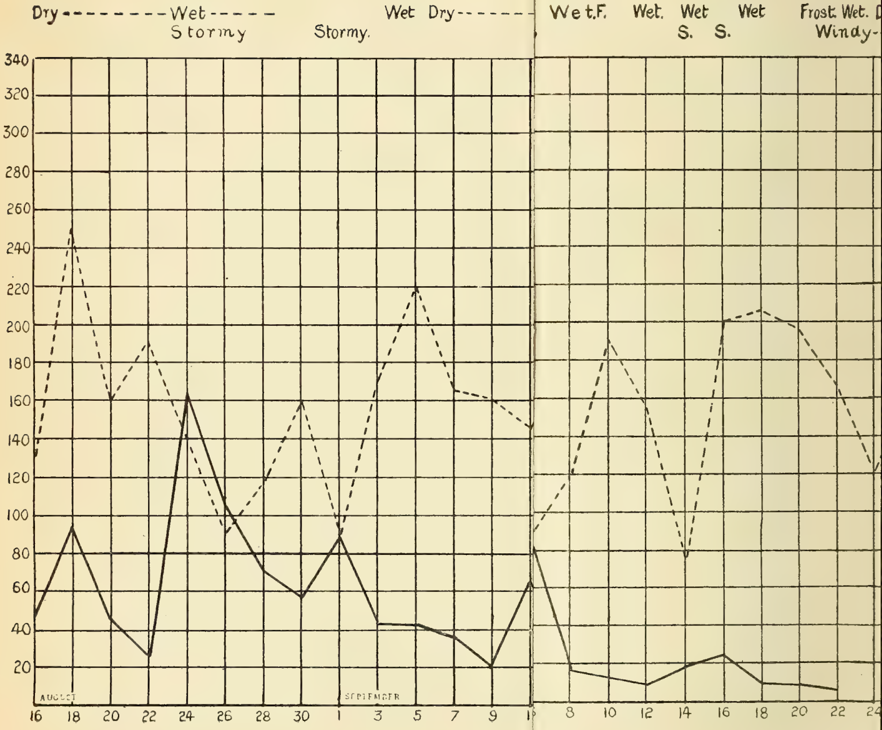
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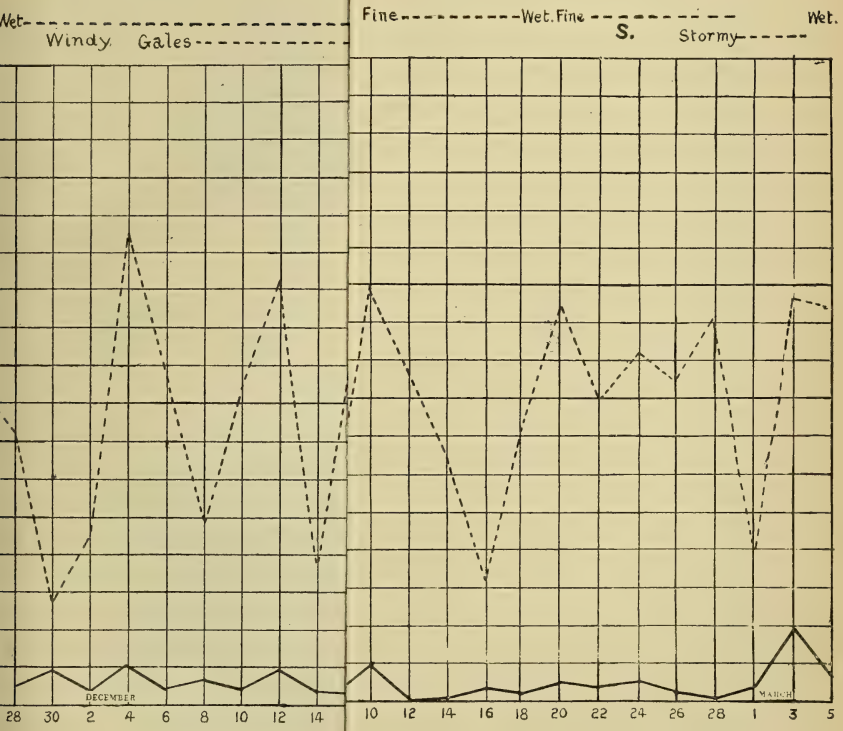

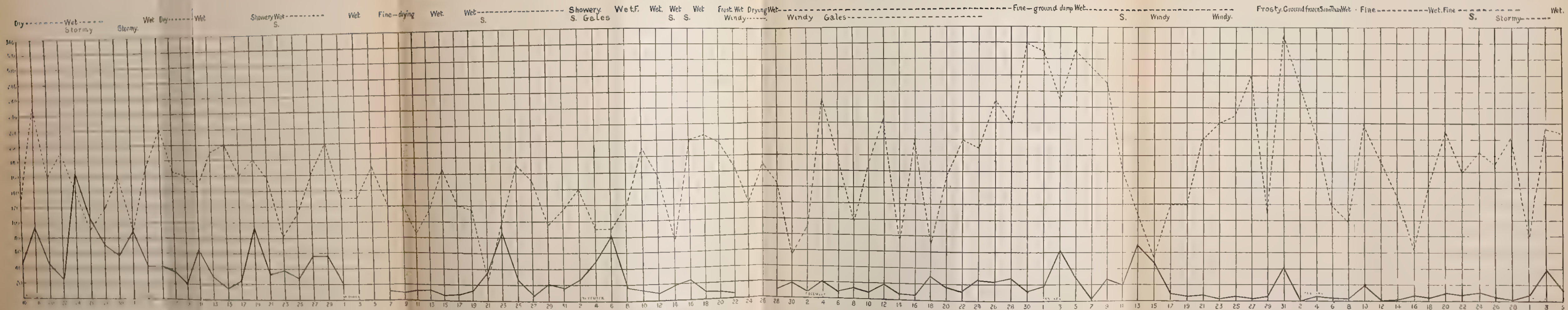
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Windy Gales------------------------
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Frosty. Ground frozen Snow Thaw Wet · Fine----------Wet. Fine ----------
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FIG. 1.

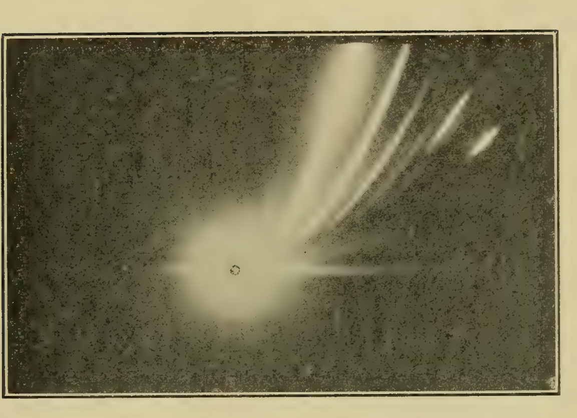
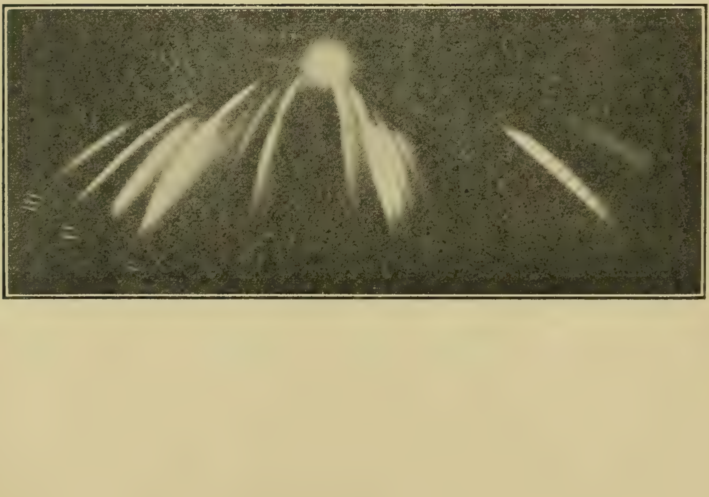
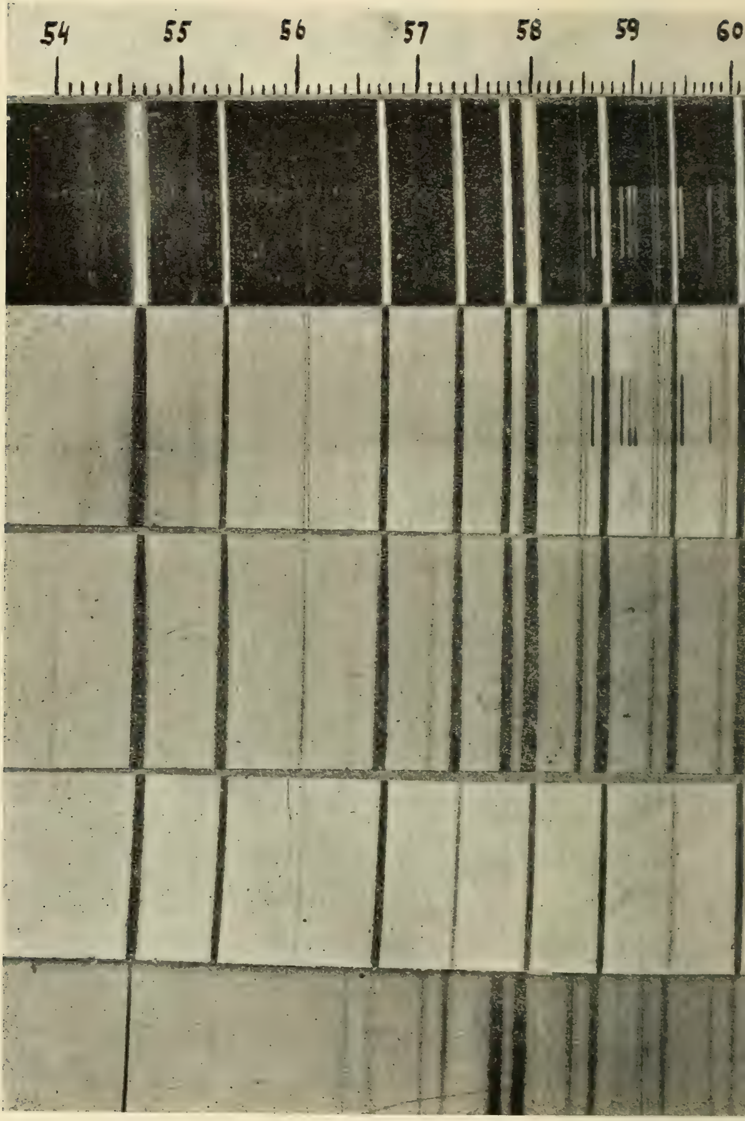


FIG. 2.

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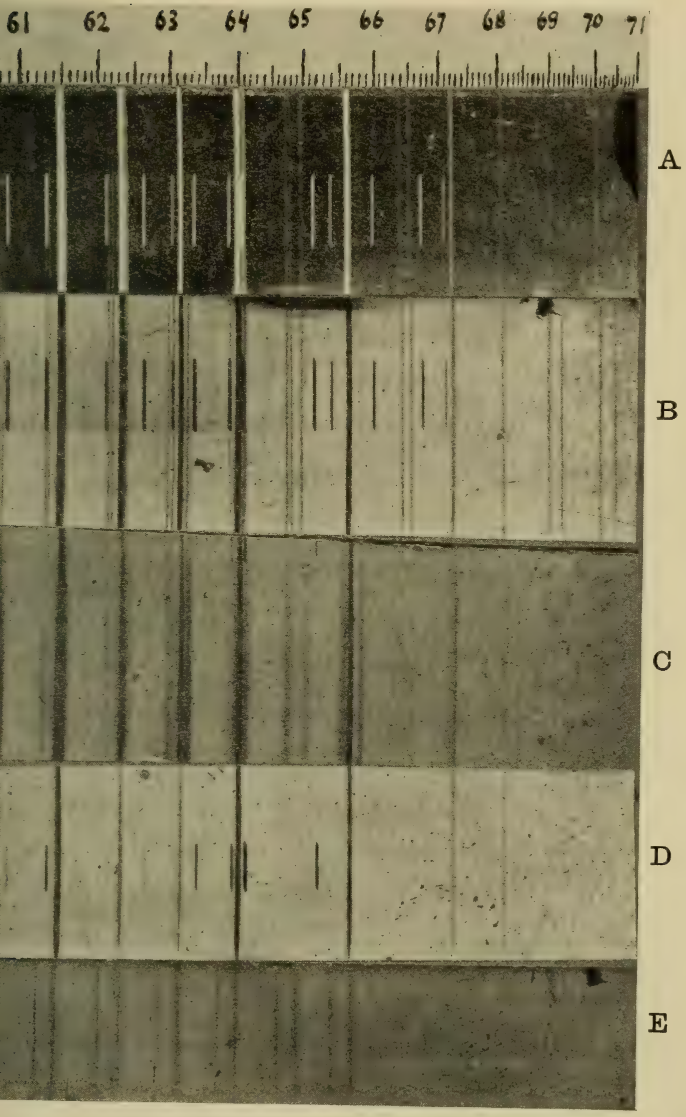

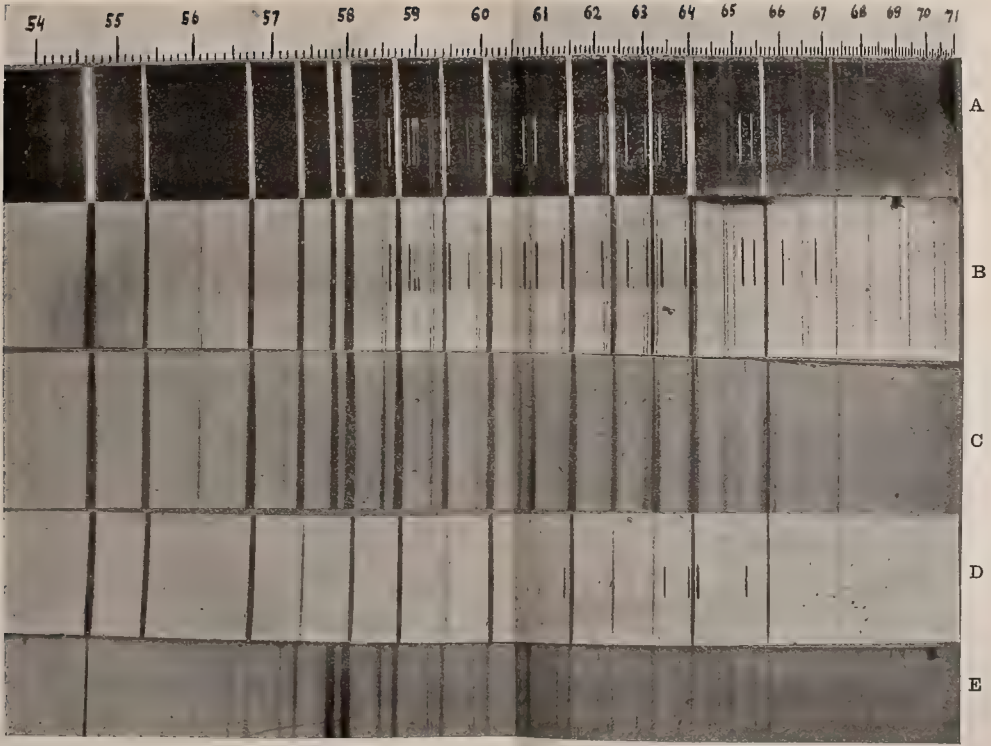
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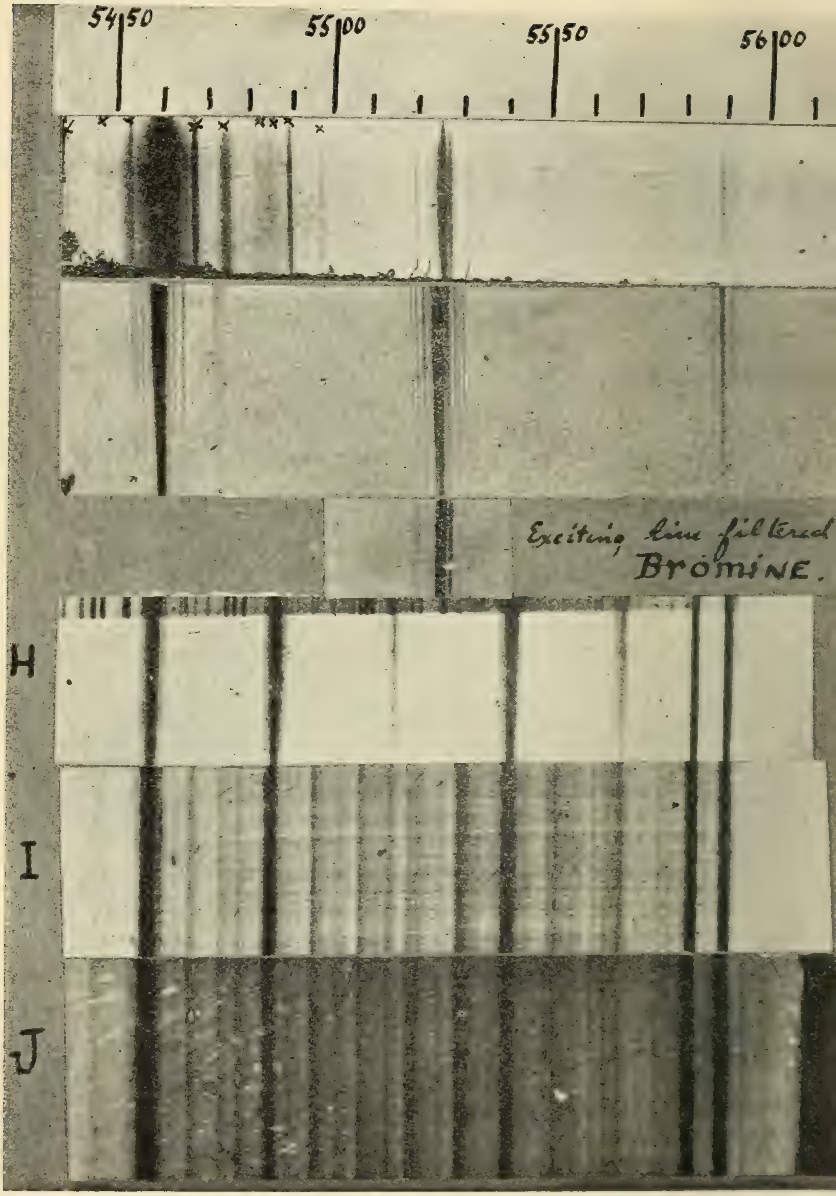
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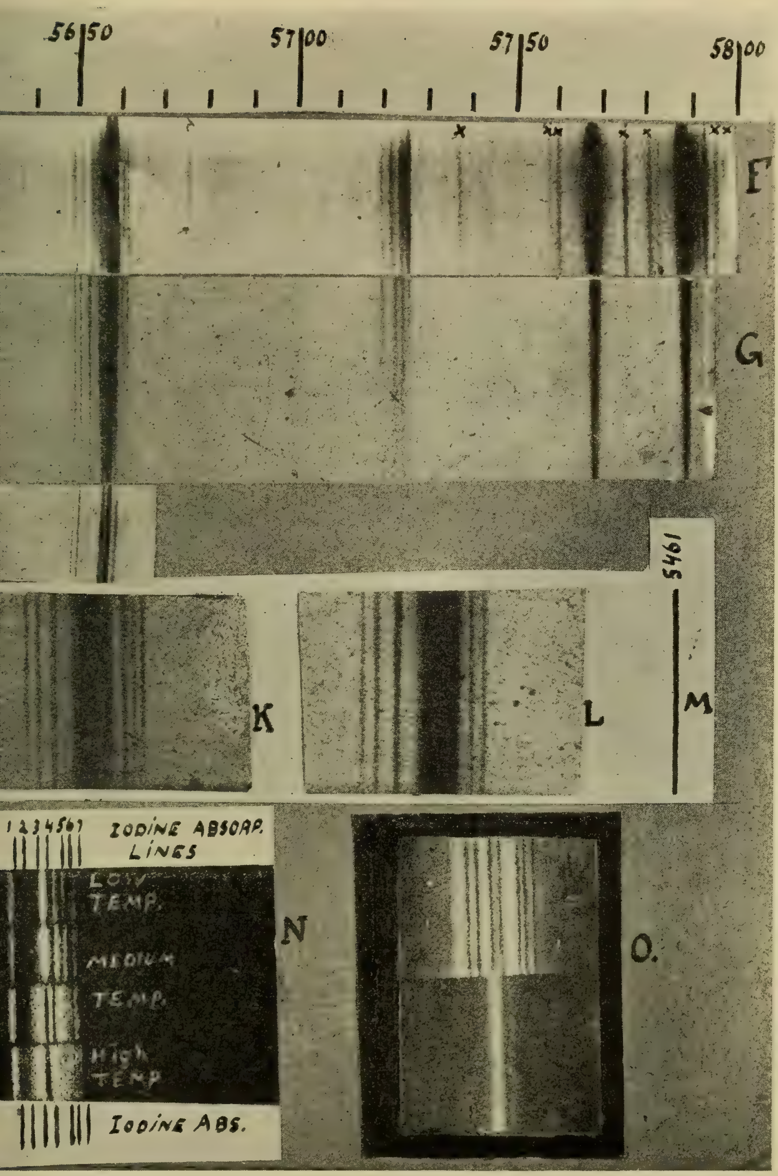
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IODINE ABS.
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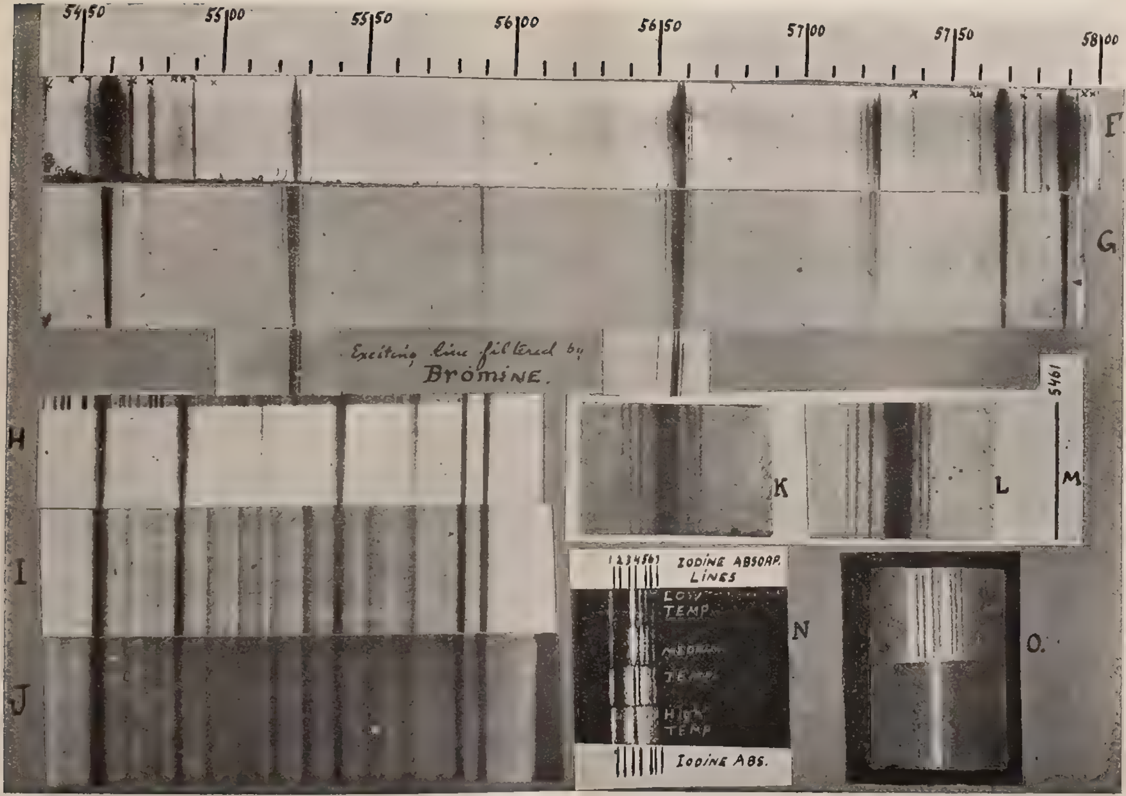
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Iodine Abs.
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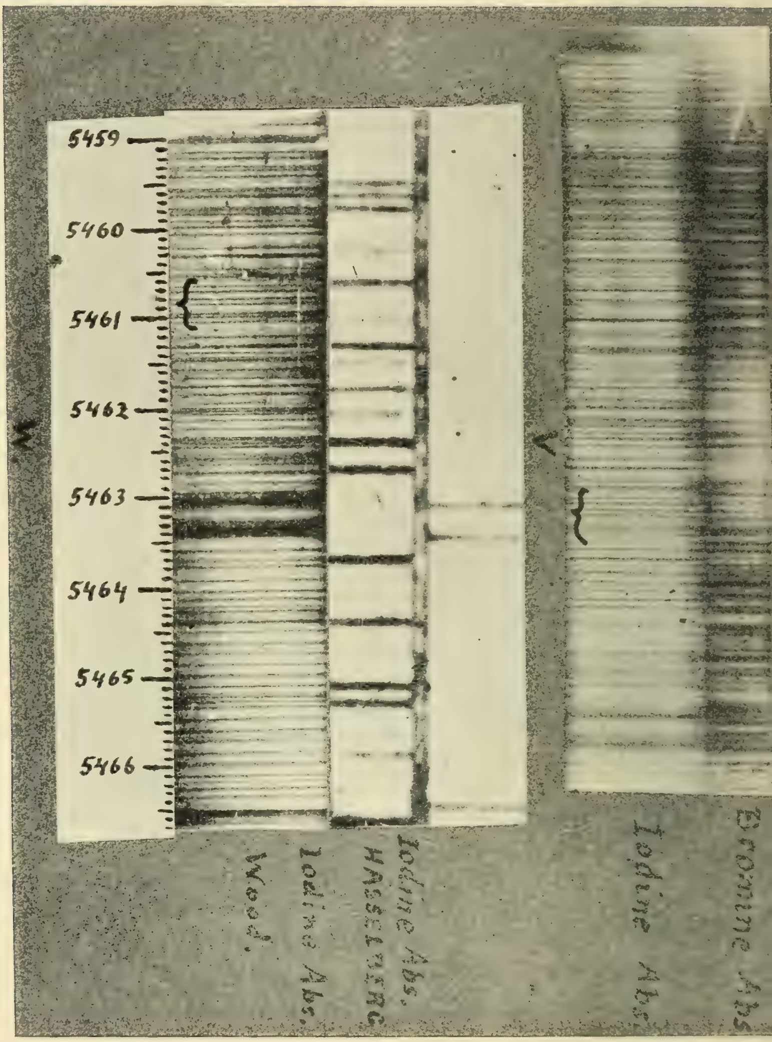
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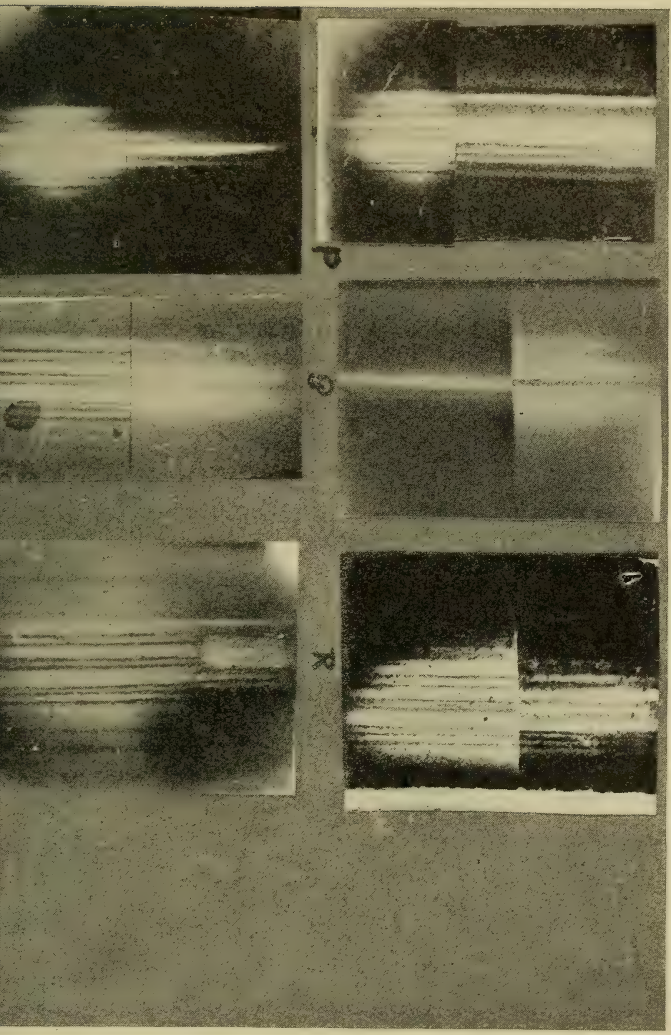
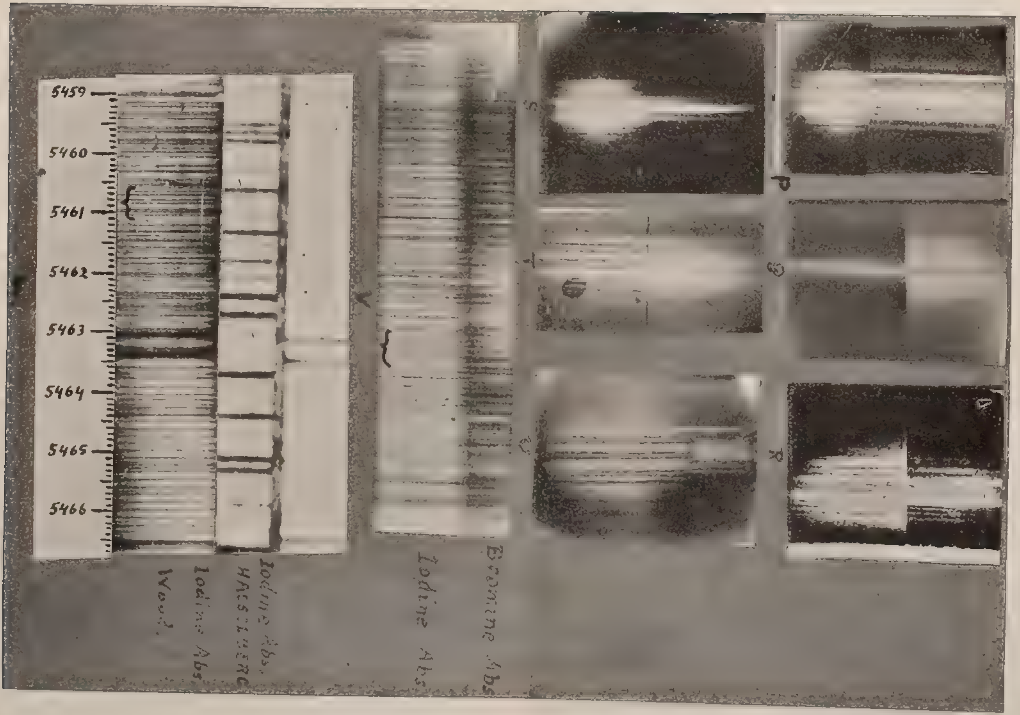
Phil. Mag. Ser. 6, Vol. 24, Pl. XVIII.

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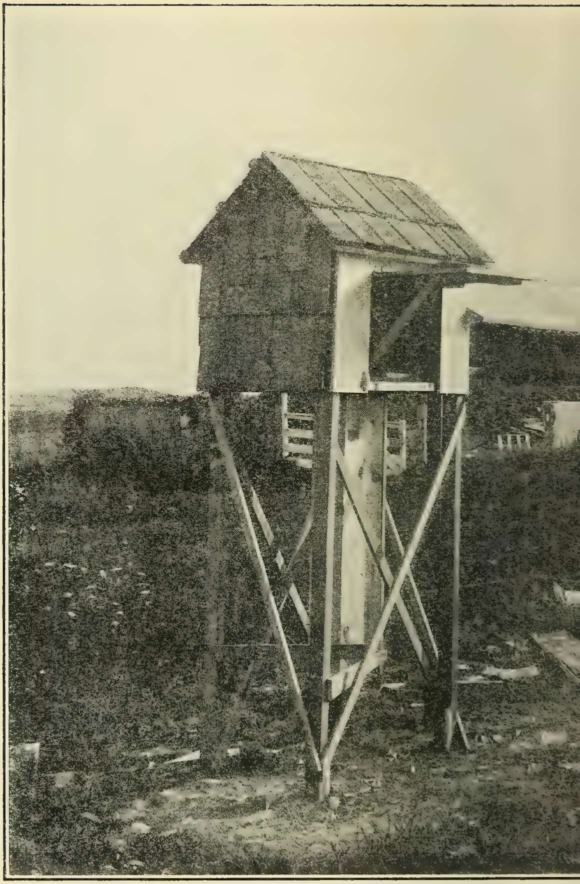

Phil. Mag. Ser. 6. Vol. 24, Pl. XIX.

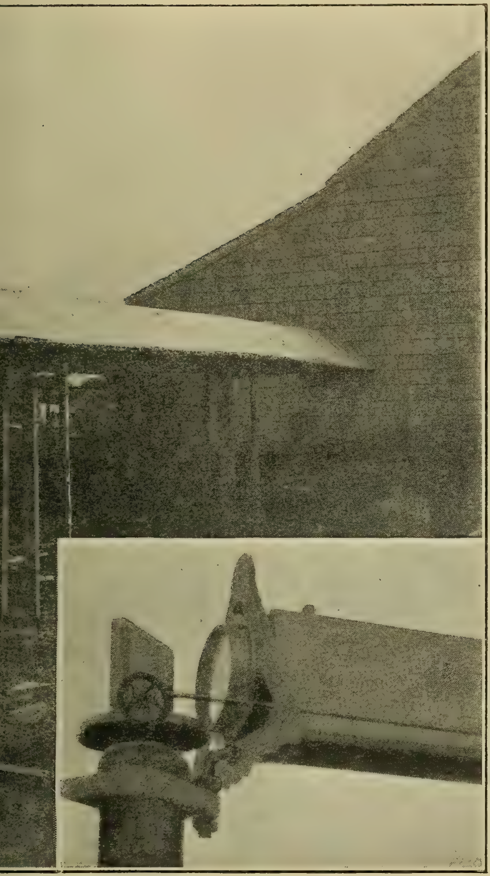

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Plate XX rec facing p. 813

THE
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PHILOSOPHICAL MAGAZINE
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JOURNAL OF SCIENCE.

[SIXTH SERIES.]

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LXXI. *The Current-Potential Curves of the Oscillating Spark and the Mechanism of Spark Conduction.* *By* S. R. Milner, *D.Sc., Lecturer in Physics, the University of Sheffield* [*].

[Plate XX.]

THE observations on the current-potential curves of the spark described below were carried out in order to test a view of the mechanism of spark conduction which I had formed as a result of a study of the streamers in the spark made a few years ago [†]. It was not until after they were finished that I found that similar work has been done by Roschansky [‡], who has made a detailed study of the voltages in the oscillating spark with different metals, spark-lengths, &c. It nevertheless seems advisable to publish a short account of my results, as they are an extension of Roschansky's in some respects, and also a knowledge of the phenomena is necessary for the theoretical considerations which follow.

The method of obtaining the curves is the well-known one of employing the simultaneous electric and magnetic deflexions at right angles of a beam of cathode rays—the electric deflexion is produced by the p.d. of the spark, and the magnetic by the spark current. The arrangement adopted is shown diagrammatically in fig. 1. The primaries of two induction-coils A and B and an automatic mercury-break C are connected in series, so that both coils are operated simultaneously by the break. At each break the coil A sends a volley of rays from the cathode D of the vacuum-tube V, and of these a narrow pencil, cut off by two metal screens E forming the anode and containing holes 1 mm. diameter, falls on the screen F and gives a bright spot of light. F is formed of powdered willemite on a glass plate, sealing-waxed to the end of the tube. The coil B simultaneously charges up a battery of leyden-jars until a spark occurs across the gap G H between spherical brass electrodes. The discharge current passes through inductance coils L_1, L_2; L_1 is arranged so that the magnetic field of the current deviates the cathode rays in a vertical plane, and the two plates X and Y in the tube so that an electric field between them gives a horizontal deviation. X, G, and E are permanently connected to earth; Y may be connected to any part of the discharge circuit H I J, or to one end of a battery of small storage-cells the other end of which is to earth, as desired. The whole tube from E to F, except the part of it facing the coil L_1, is covered with tinfoil to avoid the effects of stray electric fields.

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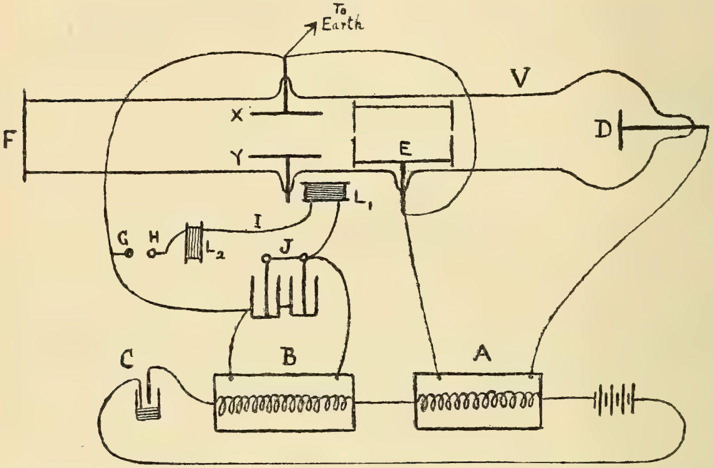
[*] Communicated by the Author.

[†] Milner, Phil. Trans. A. ccix. p. 71 (1908).

[‡] D. Roschansky, *Ann. d. Phys.* xxxvi. p. 281 (1911). See also *Phys. Zeitsch.* ix. p. 627 (1908).

Fig. 1.



When Y is connected to the inner coating J of the jars, the figure on the screen shows the spark current as ordinate plotted against the p.d. between the coatings throughout the whole period during which the rays caused by a single break of the primary current are given off from the cathode. This usually includes the period during which the oscillating spark occurs together with a little time before and after it. The curves are spirals (figs. 1 & 2, Pl. XX.). The spirals due to successive sparks do not repeat themselves exactly on the screen, and it was difficult to get good photographs by long exposures with a camera. The figures in the Plate were photographed by simply placing the sensitive plate in direct contact with the back of the fluorescent screen. There is ample light by this method to photograph the spirals due to single sparks, although naturally the definition suffers a little. The spirals are always elliptic (or circular) with their axes vertical and horizontal (the eccentricity may be altered by adjusting the position of L_1). This shows that, as theory demands, the potentials and currents are damped harmonic curves which differ in phase by 90°. The decrement of successive oscillations can be read off directly from the curves: it varies considerably with the conditions (compare the two figures), but it usually approaches more nearly to a uniform than to a logarithmic decrement*. The bright horizontal bands (sometimes mere dots) at each end of the spiral are due to the p.d. of the jars gradually rising before and after the oscillating discharge. By increasing the capacity or the spark-length, the first band may be lengthened at the expense of the second—an effect obviously produced by the resulting delay of the spark relatively to the cathode-ray emission. These bands often exhibit striations, or alternations of bright and dark portions, which show that the charge of the jars does not rise uniformly but in a series of steps—the period of these is no doubt that of the discharge of the jars through the secondary of the induction-coil.

If Y is connected to the terminal H of the spark-gap we get the spark-current plotted against the p.d. between the terminals of the gap, and the type of figure which results is shown in fig. 3, Pl. XX. The dot A represents the initial sparking p.d. and the "cross" B the current-potential curve during the oscillations. In order to see the detail here it is necessary to use a tube which gives bigger deviations for the electric field than those of the previous figures. This was done by increasing the length of the parallel plates from ·4 to 4 cm., and also putting them closer together. The curves then appear as in fig. 4, Pl. XX. The initial sparking band is now deflected off the screen (it can be brought on again with a magnet), and a distinct displacement is to be seen between the upper and lower vertical arms of the cross *. The actual course traced out by the fluorescent spot is shown diagrammatically in (*a*) of fig. 2, in which the paths in successive oscillations, in reality completely superposed, as in (*b*), are for clearness drawn one inside the other. No decrement is observable in the p.d's. of successive oscillations, but a decrement in the current of course exists, and the turning points on the vertical arms of the cross on the screen can usually be distinguished. Fig. 3 shows the deduced p.d. curve and an assumed current curve plotted with the time. At the

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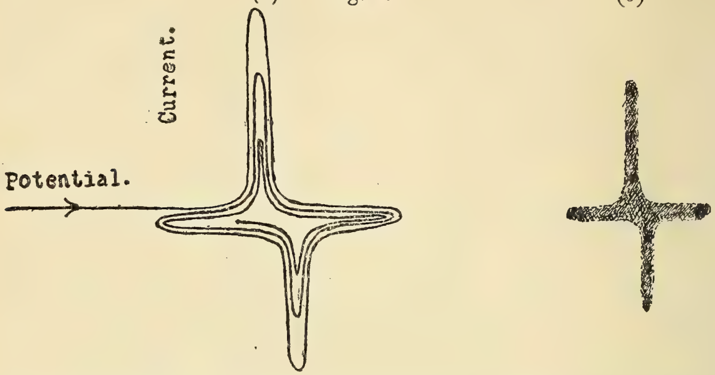
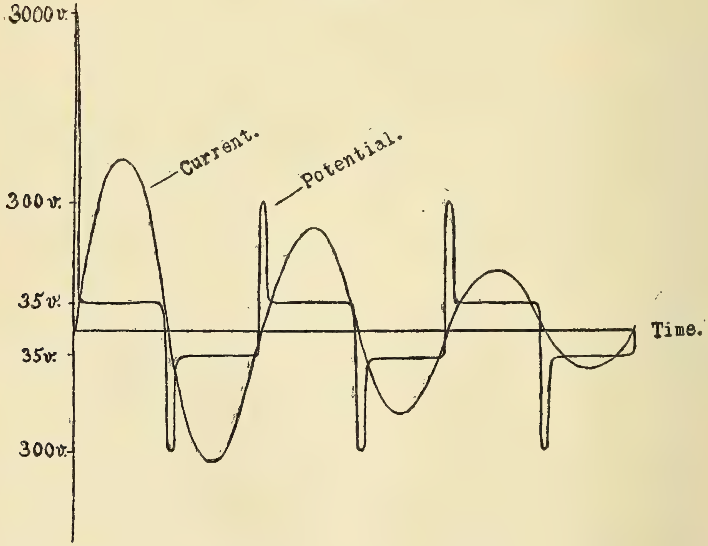
* First noted by J. Zenneck, *Ann. d. Phys.* xiii. p. 822 (1904).

Fig. 2.



(*a*) (*b*)

Fig. 3.



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* The broadness of the horizontal arms in this (and some of the other) photographs is due to the fluorescent spot having been drawn out into an elliptical one by stray fields.

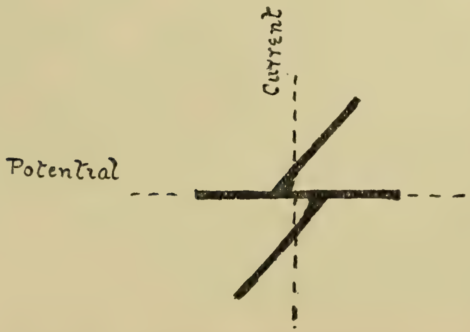
beginning of the spark, before the current has risen appreciably, the p.d. falls from the initial sparking value with great rapidity to about 35 volts; and this value is maintained constant throughout the first oscillation while any measurable current is passing. In the subsequent oscillations, for a very short period while the current is changing sign, a rapid rise of p.d. to about 300 volts occurs, followed by a fall to 35 volts again before the current has become of measurable strength. These two characteristic potential differences will be referred to subsequently as the "arc" (35 v.) and the "glow" (300 v.) p.d.'s.

Figures intermediate between the spiral and the cross can be obtained by connecting Y to I, *i. e.* between the two inductance-coils L_1 and L_2. (See fig. 5, Pl. XX.) By diminishing L_2 these become transformed more and more into the cross of fig. 4, so that there can be no doubt about the interpretation of the latter as being the form characteristic of the gap when any inductance p.d. due to the varying current is eliminated.

A large number of observations with capacities varying from ·02 to ·002 mf., and inductances varying from 500 to 3 mcrh., all showed the same general features. The variations in the magnitude of the p.d's., both the arc and the glow, are surprisingly small with the alterations in the conditions. The arc p.d. shows a slight increase with the increase of the spark-length, and probably a slight decrease at the highest frequencies attainable, while the glow p.d. is practically independent of both these conditions.

Roschansky concluded from his investigations that as the frequency is increased the spark tends to behave as a pure resistance *. In my earlier observations I found that at very

Fig. 4.



high frequencies the figures always took the form shown in fig. 4. This is obviously not a resistance effect, since the p.d. is apparently in the opposite direction to the current. At first I thought that it was an effect of the inertia of the ions in the spark-gap making itself evident when the frequency becomes sufficiently great, since on certain suppositions the inertia can be shown to give rise to this form of curve. However, closer examination showed that this was not the case, and that the effect was due to the magnetic field of other parts of the spark circuit becoming comparable with the field of the deviating coil (which at the highest frequencies was reduced to only two or three turns of wire), and thus making the resultant line of magnetic deviation not at right angles to the electrostatic one. When this effect was eliminated, no difference in character in the current-potential figures was observable down to periods of 5×10^{-7} sec. It seems to me very possible that Roschansky's results at high frequencies are capable of being explained in the same way.

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* *Phys. Zeitsch.* ix. p. 627 (1908).

Observations on the figures were made with the spark situated between the poles of an electromagnet, but no effect could be detected on suddenly switching on a strong transverse magnetic field.

A striking difference was observed when the sparks, instead of being free in air, were confined in a capillary tube. The electrodes were copper wires about 1 mm. diameter fitted tightly in the tube. There is now no clear distinction between the glow and the arc p.d's., and the average p.d. throughout the discharge is much greater than with sparks in free air (see figs. 6 and 7, Pl. XX.). The average p.d's. increase with the spark-length (compare the two figures—fig. 7 is taken under the same conditions as 6 except with a longer spark); but alteration of the inductance and capacity produces but little effect. When one electrode is enclosed in the tube and the other is free in air, there is no appreciable difference between the top and bottom halves of the curve: this shows that the p.d. is not concentrated at the electrode, but is a uniform fall over the whole length of the spark enclosed in the tube. This type of figure is probably due to the rarefaction of the air in the tube and the consequent reduction in the number of ions which carry the current; for at atmospheric pressure the effect does not show until a sufficient number of sparks have occurred to heat the tube and thereby rarify the air in the spark-gap—when the tube is partly exhausted of air by a pump the effect is shown at the first spark.

Fig. 8 shows an interesting effect which is usually observed when the plate Y is connected to I, the junction between the two inductances L_1 and L_2; the spirals thus obtained show alternations of light and dark all round at uniform intervals, indicating that the p.d. between the plates X and Y does not vary uniformly with the time but in a series of steps. The period of these agrees approximately with that calculated for the circuit formed by the parallel plates X and Y and the coil L_2, and the effect is evidently due to oscillations in this circuit superimposed on those of the main discharge. By this means oscillation periods as small as 5×10^{-9} sec. can be rendered evident and measured. Such periods are much smaller than can be measured in any other way.

Mechanism of Spark Conduction.—The general principles which govern the formation of the spark have been explained by Sir J. J. Thomson* in 1900, but they have not been applied to the condensed spark, which differs in a number of ways from the ordinary spark. We see that there are three characteristic potential differences which occur in the condensed spark, viz., the initial sparking p.d. of some thousands of volts, the glow p.d. (300 v.) between the oscillations, and the arc p.d. (35 v.) which lasts throughout the greater part of each oscillating discharge. Each of these is evidently associated with a distinct phenomenon, and the three phenomena necessary are to hand in the known theory of ionization.

Consider the conditions in the gap just before the spark occurs. In the absence of a supply of ions at the electrodes, a permanent current cannot be set up until the field reaches a value at which the positive as well as the negative ions produce ionization of the air molecules on collision. This field determines the initial sparking p.d.; and once it is reached, if it could be kept up, the ionization would increase extremely rapidly until it was practically complete. In the actual spark, however, as soon as any appreciable ionization has been produced, the field cannot be kept at its initial value, but must rapidly fall. The rate of fall of the p.d. between the spark terminals will depend on two things, viz.: (1) the rate at which the charge is carried away from the poles by the ions in the gap; (2) the rate at which the charge is brought up to the poles along the wire from the leyden-jar, and this depends on the inductance in the circuit. We have seen that in sparks in free air the p.d. falls to the arc p.d. value in a very small fraction of the oscillation period. The air is now almost completely ionized, but the high initial p.d. has another function to perform than ionizing the air in the gap; for even when the ionization is complete a permanent current cannot be carried unless there be a supply of ions at the electrodes. However, the impact of the positive ions on the surface of the cathode under the influence of the high initial p.d. will raise its temperature very rapidly: corpuscles will thus be emitted, and if the rise of temperature of the cathode surface be sufficient, the current for the rest of the oscillation will be carried through the now highly ionized air with a comparatively low p.d.

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* Phil. Mag. 1. p. 278 (1900).

The arc p.d. is partly accounted for by a drop at the cathode sufficient to keep up the temperature to the right value, and partly by the field throughout the gap necessary to make the ions carry the current. There is also probably a potential drop at the instantaneous anode, and the conditions during the main part of each oscillation are similar to those which occur in the arc discharge, but there is an important difference as regards the temperature of the anode. In the arc the anode is hotter than the cathode, a fact which is accounted for by the greater potential drop at the anode and the consequent greater development of heat there; but in the spark there is reason to believe that the anode remains comparatively cool. Even if there is in the spark a greater potential drop at the instantaneous anode than at the cathode, it will not produce the same rate of rise of the temperature of the surface layer; for there is the difference between the two electrodes that the temperature of the cathode is raised by the bombardment of positive ions, that of the anode by that of corpuscles. Now the positive ions have a large mass, and therefore a small penetrating power, consequently impinging on the surface of the cathode they will expend their whole energy in raising the temperature of a layer only a few molecules thick; while the corpuscles with their larger penetrating power will distribute their energy over a thicker layer of the anode than this. Thus although the total energy which they convey to the anode is possibly in excess of that given up to the cathode, the rate of rise of temperature of the surface layer of the anode will be less. If sufficient time were given for an approximate thermal equilibrium to establish itself throughout the whole mass of each electrode, the temperature of the anode might possibly finally become the greater, as indeed it does in the arc; but in the spark the oscillations of the discharge current are extremely rapid, and long before thermal equilibrium can be established the oscillation is over. The comparatively low temperature of the instantaneous anode in the spark forms, I think, a characteristic difference between it and the arc discharge.

This low temperature enables us to explain the occurrence of the glow p.d. between the oscillations. If the temperature of the anode were the same as that of the cathode, there is no reason to suppose that on the reversal of the current the arc character of the discharge should not remain unchanged, for the air in the gap must still be strongly ionized. But on the reversal of the current at the first instant what is now the cathode is comparatively cool, and it cannot supply the necessary corpuscles at a sufficient rate. Since the air in the gap is already ionized, we have now the exact conditions necessary for the glow discharge. By the removal of the negative ions from the neighbourhood of the electrode, the potential drop becomes concentrated in that region until it reaches such a value that the positive ions ionize the air there, giving the necessary supply of negative ones at the electrode. In the rest of the field at this potential only the negative ions will be able to ionize. The approximate agreement of the glow p.d. with the cathode fall of potential in vacuum-tubes, and its constancy under varied conditions, confirms this explanation of it. The glow p.d. must be of very short duration, for the new cathode is now being bombarded by the heavy positive ions, its surface rapidly rises in temperature, and when sufficient corpuscles are emitted to convey the current from the electrode to the gas, the arc period supervenes.

We shall now consider briefly a number of features of the spark which are elucidated by this view.

1. *The Core and Sheath.*—The condensed spark in air exhibits a very bright white central part or core, surrounded by a much less bright sheath or aura. On the view taken above, the core marks the region of the spark in which the initial ionization by positive ions occurs. The maximum field naturally occurs only at the centre of the spark, surrounding this there is a region in which the field is only sufficient to produce ionization by negative ions, and the sheath may be associated with this region*. If we consider a series of sparks in which the self-induction of the circuit is gradually diminished from large to very small values, at the larger inductances there is no differentiation of the spark into core and sheath; then the core forms, and gradually grows brighter and brighter up to a certain point, after that its width begins to increase, its intrinsic brightness remaining as far as can be judged constant. In fig. 9, Pl. XX., photographs of a series of sparks, 7 mm. in length, and

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* The glow discharge in the oscillations no doubt also contributes to the sheath.

from a capacity of ·0055 mf. with gradually diminishing inductances, are shown, which exhibit these effects. They are easily explained qualitatively in terms of the above theory. The brightness of the core may be taken as proportional to the amount of ionization per c.c. of the air produced by the initial sparking p.d., the more slowly the initial p.d. falls to the arc value the greater will be the final ionization produced, and we have seen that the slowness of this fall will increase as the inductance in the discharge circuit is diminished. The fact that after a certain point the thickness of the core begins to increase suggests that at this point the ionization of the air is approaching completion, and that any further increase in the discharge current then necessitates an increase in the cross-section of the region in which ionization takes place. This is confirmed by the following table, in which the diameter of the core and the calculated value of the density of the average spark current, assuming that it is concentrated into the core, are given for a series of sparks with different inductances similar to those of fig. 9. The average current is taken as charge of jars÷half period$=30{,}000 l\mathrm{K}/\pi\sqrt{\mathrm{LK}}$, where $l=$ spark-length, ·335 cm., $\mathrm{K}=$ capacity of jars, ·0055 mf., $\mathrm{L}=$inductance.

Inductance. mcrh.	Average Current. amp.	Thickness of Core. cm.	Current Density. amp./sq. cm.
320	13	0·03	18600
170	18	0·03	26000
95	24	0·03	34500
40	38	0·03	54000
15·6	60	0·04	47500
10·0	75	0·045	48000
5·0	106	0·05	54000
2·7	140	0·06	50000
Conn. wires only.	—	0·095	——

It will be seen that the average current density reaches a limiting value of 50,000 as the inductance is diminished *. The maximum current density would be $\pi/2$ times as great as this. A rough calculation shows that the limiting density is of the same order as that which would occur in completely dissociated air. This would be

$$\mathrm{C}=\mathrm{N}e\mathrm{VF},$$

where N is the number of molecules per c.c. of the air in the

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* In another set of sparks ·68 cm. long the limiting current density 55,000 was obtained, in a third set ·2 cm. long the value was only 20,000.

spark-gap, e the ionic charge, V the velocity of the negative ions, F the field, and the small fraction of the current carried by the positive ions is neglected. N is unknown at the temperature of the spark, but we can approximately take NV as uninfluenced by changes of density and temperature, and assume for it the same value as for the negative ions in flames. At 1800° C., N would be $2{\cdot}75 \times 10^{19} \times 273/2073$; and according to the measurements of Gold[*], V in flames at 1800° lies between 8000 and 13,000 (say 10,500) cm. per sec. per volt per cm. Also $e = 1{\cdot}57 \times 10^{-19}$ coul., and for F we may put the rate of increase of the arc p.d. in the spark with the spark-length. This has been measured by Roschansky for numerous electrodes, and averages 10·5 volts per cm. With these values we get

$$C = 63{,}000 \text{ amp./sq. cm.}$$

as an estimate of the maximum current density which the air is capable of carrying with the field which exists in the spark. This is of the same order as the experimental number, and no more is of course to be expected.

2. *Spectra of Core and Sheath.*—The three spectra in fig. 10, Pl XX., are those of the image of a horizontal spark between copper electrodes thrown on the vertical slit of a spectroscope. They refer to sparks with a capacity of ·017 mf., and inductances of 1·3, 40, and 170 mcrh. respectively. An examination of (*a*) shows that some of the lines (such as that marked α, the hydrogen line 6563) are distinctly longer than other lines (*e. g.* β, the nitrogen line 5003), even though the latter may be the stronger of the two. The short lines represent the spectrum of the core of the spark, the longer those which exist in the sheath as well (the very long lines are due to Cu vapour from the electrodes). The line of demarcation is really more distinct than appears in the photographs, since the exposure required about 20 sparks, and their images cannot all be made to fall on exactly the same place on the slit. As the inductance is diminished the core lines diminish in length (fig. *b*) as the core diminishes in diameter; and they finally disappear altogether, leaving the spectrum shown in fig. *c*, which is quite different from the core-line spectrum. An account of the last spectrum, which corresponds to such inductance that there is no differentiation of the spark into core and sheath, is given by Hemsalech[†], who has called it the "second air-line" spectrum.

That there would be a difference in the spectra of the core and the sheath might be expected as a result of the different ionizing agents in the two cases. The impact of a positive ion on a molecule might be expected, in consequence of its greater mass and the probably greater amount of energy which it communicates to the molecule, to produce a different type of vibration in the ion formed from that resulting from the impact of a corpuscle. That the essential feature for the production of the core lines is the impact on and ionization of the air molecules by positive ions is proved by an observation made in 1884 by Schuster *, who showed that the line spectrum of air (*i. e.* that of the core of the spark), is seen in the glow which covers the cathode in vacuum-tubes. This is a region in which ionization by positive ions is now known to be occurring and in which the production of the lines cannot be attributed to the current density or the temperature, which are both comparatively low. With regard to the second air-line spectrum Hemsalech discovered that, unlike the core spectrum, it occurred in the oscillations subsequent to the first discharge. This effect allows us to associate it definitely with the glow discharge (ionization by negative ions) which we have seen occurs in the interval between the oscillations.

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[*] Proc. R. S. lxxix. p. 43 (1907).

[†] Hemsalech, *Comptes Rendus*, clii. p. 1007 (1911).

3. *Nature of the Streamers.*—The inclination with respect to the axis of the spark of the luminous streamers which are seen when the spark is viewed in a rotating mirror, shows that the luminosity of the electrode-metal vapour occurs at the centre of the spark at a later instant than near the poles. Schuster and Hemsalech from their researches † came to the conclusion that the reason of this delay was that the metal of the poles was vaporized and rendered incandescent by the heat of the spark, and that the vapour takes an appreciable time to diffuse from the poles to the centre of the gap. Schuster and Hemsalech's observations, however, only apply to the inductionless spark, where the streamers corresponding to the successive oscillations are all massed together and superposed on each other in the photographs. Their conclusion therefore does not strictly apply to the individual streamers in the successive oscillations of the discharge. Royds ‡, from an extension of their work to sparks with induction in circuit, concluded that it is in the case of the first streamer only that the inclination represents the velocity of diffusion of the vapour, and that in the subsequent ones it represents the rate of propagation through a comparatively

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* Schuster, Bakerian Lecture, Proc. R. S. xxxvii. p. 317 (1884).

† Phil. Trans. A. cxciii. p. 189 (1900).

‡ Phil. Trans. A. ccviii. p. 333 (1908).

stationary vapour of some form of luminosity caused by the discharge current. Similar work of my own * resulted in a conclusion more in accordance with the original view of Schuster and Hemsalech, that each streamer is the drawn-out image of a puff of luminous vapour given off from the electrode at each oscillation and proceeding at a high rate towards the centre of the gap. It was found that the metal vapour is in many cases (if not in all) electrically charged, and it is thus in addition to diffusion impelled towards the centre of the gap by the electric field of the spark.

If we accept this view of the constitution of the streamers, the results of the present paper go to show that the electrical propulsion of the vapour is not likely to account for very much of the velocity which the streamers exhibit, for the arc p.d. which lasts throughout much the greater part of the oscillations is a comparatively small one, and the glow p.d., which might be expected to produce an effect if it lasted, is of excessively short duration. We must consequently infer that the main cause of the production of each streamer is the high temperature to which the surface of the electrode is raised by the impact on it of the ions which carry the current across the gap. The theory of the mechanism of conduction in the spark given above now enables us to explain the often noted but unexplained fact that the streamers do not show with equal intensity at each electrode, but that in successive oscillations they are alternately more prominent at one electrode than at the other. The more prominent streamer is thus always associated with an electrode of the same sign, which according to the observations of Schenck †, Walter ‡, Royds, and Milner, is found to be negative. Now we have seen that in consequence of the different penetrating powers which we must ascribe to the positive and negative ions, combined with the rapidity of the oscillations, the characteristic feature of the spark which distinguishes it from the arc is the comparatively low temperature of the surface layer of the instantaneous anode. The strength of the streamer is conditioned by the temperature of the surface layer only of the electrode, and it should therefore be greater at the instantaneous cathode, as is found to be the case.

August 8th, 1912.

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* Phil. Trans. A. ccix. p. 71 (1908).

† Astrophys. Journ. xiv. p. 116 (1901).

‡ *Ann. d. Phys.* xxi. p. 223 (1906).

LXXII. *Recoil Atoms in Ionized Air.* By Alois F. Kovarik, *Ph.D., Assistant Professor of Physics, University of Minnesota* *.

WHEN a radioactive emanation disintegrates, the atom of the newly formed substance may be drawn to a negatively charged electrode. This was investigated by Rutherford and others. Rutherford † also measured the velocity in air of the atoms formed from radium emanation and from thorium emanation, and found these to be the same as the velocity of the positive ion in air. Schmidt ‡ has shown that the Ra A atom behaves like a positive ion in air. The recoil experiments of Hahn and Meitner § show that the atoms formed after the disintegration of other radioactive substances are also drawn to the negative electrode in an electric field. Franck ‖ using the recoil atoms, thorium D, showed that their velocity in an electric field was the same as that of the positive ion in the corresponding gas. It therefore appears that the recoil atoms of all disintegrating radioactive atoms behave like positive ions in the same gas. A theory attempting to explain these results has been put forth by Wellisch ¶.

The present experiments were undertaken principally to ascertain if the recoil atoms could be collected on a negatively charged electrode when the air between the plates of the field was strongly ionized. From the experiments referred to above, one would anticipate that the number of atoms drawn to the negative electrode through ionized air would diminish with the intensity of the ionization on account of the neutralization of the charge of the atoms with the negative ions of the air. The results of these experiments confirm this idea. Wellisch and Bronson**, however, in some of their recently published experiments, come to the conclusion that the effect of the Röntgen rays passing through a gas in which the recoil atoms, Ra A, were collected was appreciable only when the activity and ionization were far from saturation.

An investigation was also made showing that the number of recoil atoms drawn to the negative electrode increased as the potential difference between the plates was increased, the distance remaining constant; and also, that the number increased as the distance was decreased, the potential difference being constant. In these experiments no external ionizing agent was employed. Recoil experiments were also made using plates of different polish for the active deposit plates from which the recoil atoms were ejected. The number of recoil atoms collected on a negatively charged electrode was greater from the surfaces of higher polish.

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* Communicated by Prof. E. Rutherford, F.R.S.

† Rutherford, Phil. Mag. v. p. 95 (1903).

‡ Schmidt, *Phys. Zeit.* ix. p. 184 (1908).

§ Hahn and Meitner, *Verh. D. Phys. Ges.* xi. (3) p. 55 (1909).

‖ J. Franck, *Verh. D. Phys. Ges.* xi. (19) p. 397 (1909).

¶ Wellisch, *Ver. D. Phys. Ges.* xiii. p. 159 (1911).

** Wellisch and Bronson, Phil. Mag. xxiii. p. 714 (1912).

These experiments were carried out two years ago in Professor Rutherford's laboratory. It was the hope of the writer to continue them, but after leaving England it was found impossible to do so at once. Since work in this particular field is at present attracting other investigators, it was decided to publish the results obtained in these preliminary experiments.

Experimental Method.

The experiments consisted in collecting actinium D by recoil from the actinium active deposit. The air through which the recoil atoms had to pass was ionized by the α-particles from radium emanation and its products enclosed in a glass tube whose walls were thin enough to permit the α-particles to pass through.

Two metal plates, large enough to ensure a uniform field at the centre, were held apart by an ebonite plate having a circular hole through the centre. The size of the hole was the same for all the distances used. The lower of the two plates was exposed to actinium emanation, so that the area of the active deposit was considerably smaller than the opening in the ebonite. In the recoil experiments the lower plate was charged positively, while the upper plate, which served to collect the recoil atoms, was charged negatively. The exposure to the actinium emanation was at least five hours with a potential difference of about 200 volts. In order to be certain that the amount of the active deposit was the same in all the experiments, the α-radiations and the β-radiations were measured at convenient times and their values reduced to the time of removal from the emanation. These values, respectively, did not vary more than 8 per cent. for the different experiments. It was found necessary to use the same plate on which to collect the active deposit in all the experiments.

The time for the exposure in the recoil experiments was twelve minutes, starting immediately after removing the plate with the active deposit from the emanation. The plate with the actinium D obtained by recoil was then placed in a definite position under a β-ray electroscope, and a decay curve was taken for the actinium D. The sensitiveness of the electroscope was checked in each experiment by means of the β-rays from a uranium oxide standard. The ratio of the activity of actinium D at zero time divided by the activity of the standard, gave the measure of the number of recoil atoms collected on the negative plate.

In the experiments with the ionized air in the field, a small glass α-ray tube containing radium emanation in equilibrium with the active deposit was fixed in a definite and permanent position between the plates. The average range of the α-particles in the air outside the tube was about 3 cm., and this was sufficient to traverse all the air between the plates.

Actinium D drawn through Ionized Air.

In these experiments measurements were made from time to time as the radium emanation in the α-ray tube decayed. The strength of the emanation was a measure of the ionization between the plates. Two series of measurements were made and were found to be in good agreement. The one in which the original amount of the radium emanation used was the greater is given in this paper. The initial amount of emanation in this case was 10 millicuries. The distance between the plates was 12·3 mm. The potential difference between the plates was 115 volts, which was sufficient to produce an approximate saturation of the current due to the radiations from the active deposit. Table I. gives the results of the experiments. The

TABLE I.

Relative amount of Emanation.	Actinium D by recoil.
100·0	12
94·2	12
80·5	16
55·3	17
46·5	22
40·4	24
26·3	29
16·1	30
13·0	31
11·5	35
9·6	34
7·5	42
5·2	51
3·7	63
2·2	66
1·8	77
1·27	81
0·65	86
No emanation.	100

strength of the emanation—which served as a measure of the ionization—is taken as 100 for the first experiment, and the subsequent values were calculated from the decay of the emanation. These values were, however, checked occasionally by comparing the γ-radiation with that from a radium standard. The number of actinium D atoms on the plate, as measured by the β radiation from the atoms disintegrating, was taken as 100 when the α-ray tube contained no emanation.

It will be noticed that as the ionization decreases the relative number of actinium D atoms drawn to the negative plate through the ionized air increases.

When no external ionizing agent was used, the α-particles from the actinium active deposit (about 2×10^6 per sec.) produce some ionization. Besides this ionization there is also a considerable ionization produced by the recoil atoms themselves *. When this ionization was increased by means of a weak polonium plate (10^5 α-particles per sec.), no perceptible decrease in the amount of actinium D collected was noticed. The 10 millicuries of radium emanation produced about 10^{14} ions per second in the air between the plates.

When the potential difference was changed (the air being strongly ionized), an increase was accompanied by an increase in the amount of actinium D collected, while a decrease produced a decrease in the amount of actinium D. It is quite evident that with a very high potential difference the time for the ions and also for the recoil atoms to cross the field is small and, no doubt, the path more rectilinear. Hence the chance of recombination is smaller.

Changes of Potential Difference and of Distance between the Plates.

Experiments were also carried out by changing the potential difference between the plates keeping the distance constant, and by changing the distance keeping the potential difference constant. In these experiments no external ionizing agent was employed. The results are given in Table II. (p. 726).

The results obtained are in good accord with the view that the recoil atoms lose their charge by recombination like positive ions. With no potential difference the actinium D collected is no doubt due to diffusion. When the distance between the plates was 12·3 mm., only a trace of actinium D

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* Wertenstein, *Le Radium,* ix. p. 6 (1912).

TABLE II.

Distance 12·3 mm. | Potential Difference 115 volts.

P.D. in volts.	Actinium D by recoil.	Distance in mm.	Actinium D by recoil.
0	trace		
10	4·9	0·2	100·0
13·5	13·8	6·3	91·2
20	34·1	11·5	86·2
30	55·6	12·3	80·5
50·5	74·5	16·0	74·2
70	85·5	22·5	43·5
110	87·0	32·0	11·1
207	100·0	......	......

was observed, while with a distance of only 0·2 mm. the amount was readily measured, and was about 3 per cent. of that obtained with a strong field. With a distance of 0·2 mm. two volts produced approximate saturation.

Effect of the Surface of the Plate used for the Active Deposit.

It was noticed during the progress of these experiments that the same amount of actinium D by recoil was not obtained when the active deposit was collected on different plates. This was found to be due to the surface of the plate. Wertenstein[*] has recorded a similar observation. The figures in Table III. will show the importance of the "polish" of the surface.

TABLE III.

Plate.	Actinium C by recoil.
1	100
2	92
3	78
4	62

The plate No. 1 was smooth tinfoil on glass. It gave the best results. Plate 4 was a copper plate roughened by means of emery-paper. Plate 3 was a smooth copper plate, and plate 2 was No. 3 polished to some extent by means of rouge.

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[*] L. Wertenstein, *Le Radium*, vii. p. 288 (1910).

The following explanation of this phenomenon seems probable. The distance that the atoms recoil in air is only a small fraction of a millimetre at atmospheric pressure. Since the path is equally probable in all directions, many of the atoms are projected along or close to the surface of the plate ; and if the plate has any projections, however small, some atoms will strike them and either lose their charge or adhere to the plate, so that they fail to be drawn to the negative plate. With smooth plates fewer atoms are so obstructed in their path.

Under the most favourable conditions in air at atmospheric pressure, the amount of actinium D obtained by recoil was less than one-half of the theoretical maximum deduced from the β-ray measurements of the active deposit. The distance between the plates was 0·2 mm., and the potential difference was 1000 volts. Exposure for the recoil was 30 minutes. The value of the β-radiation from the actinium D collected by recoil was reduced to the time of the removal of the plate from the field. About a half-hour later the β-radiation from the active deposit was measured, and its value was reduced to the same time. The relation of the β-ray activities of the actinium D obtained by recoil to that in the active deposit was 23 per cent. Since only one-half of the atoms recoil into the air above the plate, the maximum amount expected would be 50 per cent. Hahn and Meitner (*loc. cit.*) obtained a somewhat higher ratio, and Wertenstein (*loc. cit.*) working on RaB obtained practically the whole amount to be expected theoretically. It seems very unlikely that this low value is due entirely to the imperfect surface of the plate used for active deposit, and to the neutralization of the charge of the atoms in the gas ionized by the radiations from the active deposit and the recoil atoms.

From a large number of decay curves taken during these experiments, the half-period [*] of actinium D was found to be 4·71 minutes [†].

In conclusion I wish to express my thanks to Professor Rutherford for his interest in the experiments and for supplying me with the necessary radioactive materials.

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[*] Alois F. Kovarik, *Phys. ZS.* xii. p. 83 (1911).

[†] Some experiments on the recoil atoms, thorium D, were also carried out. The mean value obtained for its half-period is 3·07 minutes, which is practically the value found by v. Lerch.

LXXIII. *Dust Figures produced by Electric Sparks. By* Edwin H. Barton, *D.Sc., F.R.S.E., Professor of Experimental Physics, and* Walter B. Kilby, *B.Sc., Research Scholar, University College, Nottingham*[*].

[Plates XXI. & XXII.]

THE problems of dust figures have recently attracted considerable attention, papers on the subject having appeared by T. J. Richmond[†], by J. Robinson[‡], and by Marsh and Nottage[§].

As a result of these investigations, the quantitative relation between the relative pitches of the striæ and the intensities of the air currents producing them may be regarded as established. But there still appeared room for much further work of a varied qualitative character. We accordingly set out to obtain, where possible, dust figures exhibiting in turn the effects of waves which suffered reflexion, refraction, interference, and diffraction. As the experiments progressed other lines of work suggested themselves and were followed up, frequently with interesting results.

Out of the many experiments tried photographs of twenty of the figures are here given. But, before passing on to consider these in detail, it may be well to indicate in outline the chief results obtained, which are as follows:—

1. *Reflexion* from a concave mirror showed a distinct focus. Separate exhibition of the incident and reflected beams was not secured.
2. *Refraction* was shown where the waves passed under a cover plate.
3. *Interference* effects were clearly exhibited in the space between two spark-gaps.
4. *Diffraction* was obtained under a variety of circumstances.
5. *Whispering-gallery* effects were shown distinctly, both when specially sought and also as subordinate features in many other cases.
6. *Variation of Pitch* of the striæ with the intensity of the disturbance producing them was clearly exhibited.

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[*] Communicated by the Authors.

[†] Phil. Mag. pp. 771–782, Nov. 1909.

[‡] Phil. Mag. pp. 180–187, July 1909; pp. 476–485, April 1910; pp. 268–270, February 1911.

[§] Proc. Phys. Soc. of London, pp. 264–276, vol. xxiii. part iv. June 15, 1911.

7. *Creeping of Striæ* in tubes, both from and *towards* the spark, was observed and sometimes it occurred both ways simultaneously.
8. *Inclination of Striæ* in tubes produced by the spark was obtained by the simultaneous sounding of a tuning-fork.

Experimental Arrangements.

The Surfaces.—The dust figures in the present work were usually obtained on the surface of plate-glass placed horizontally. This offered the advantage of a surface practically plane, but being hygroscopic it needed careful drying and cleaning. Plates of steel and brass were occasionally tried and, though capable of a high polish, often gave trouble by a persistent though almost imperceptible curvature.

Sometimes a cover of plate-glass was used to confine the energy of the spark disturbance, thus securing cylindrical instead of spherical radiation. In special cases tubes were used instead of the plate, thus securing linear radiation in the space under test.

The Powders.—Twenty different powders were tested, but most of them rejected for one fault or another. Thus, aluminium and borax were too irregular in the shape of the grains. The following were rejected on account of irregularity in size of grains:—basic slag, bath-brick, black oxide of iron, charcoal, cork filings, and pepper. A number of powders were rejected because the separate grains clotted together into a large cluster. This class comprised black-lead, boric acid, corn-flour, flour, flowers of sulphur, French chalk, plaster of Paris, rouge, and starch. Red lead was difficult to shift owing to its high density and was prone to clot. Iron filings are usually irregular as well as dense, but their magnetic properties seemed helpful and some figures were obtained with them.

Lycopodium spores seemed by far the best powder to use for these figures. The separate spores are almost identical in size, nearly spherical in shape, and show only a very slight tendency to adhere together. To dust the surface, the lycopodium was well dried, a cloud of it thrown from a pepper-box, and then the clean, dry plate passed into the cloud, after the subsidence of any stray clots which might be initially present. The repetition of this process of dusting for five or six times usually gave a sufficient sprinkling to form the basis of a dust figure. Because of its excellence lycopodium was used practically throughout.

The Sparks.—The electric sparks used for producing the dust figures occurred vertically between two balls or a ball and very blunt point. The spark-gap was usually of the order 2 cm., but was varied slightly according to the degree of confinement of the disturbance by cover-plate or obstacles. To ensure a sufficient quantity of electricity passing at each spark, a leyden-jar was always used across the terminals in shunt with the spark-gap. This jar was small, medium, or large according to the requirements of the case.

The number of sparks needed to produce a figure varied with circumstances. In any case it was found that the figure reached its best state at a certain stage.

The sparking potential was obtained by an influence machine or an induction-coil, the former being more suited for certain patterns and the latter for others.

A small spark-gap was arranged on the prong of a large tuning-fork of frequency 128 per second. Sparks were then passed while the fork was vibrating, the figures being examined in a horizontal tube with one end near the spark. But the fork's vibrations appeared to have no decided effect on the striæ.

An explosion of soap bubbles (blown with mixed hydrogen and oxygen) was also tried near the end of a dust-tube, but failed to produce any striæ.

Shadowgraphs and Enlargements.—Where the dust figures were formed on a glass plate and a print the same size was desired, the following method of photography without a camera was found suitable. The photographic plate was placed film-side down close over the dust figure, separation being secured by several microscope-slips. An electric light about six feet below then gave the desired photograph with a few seconds' exposure.

Where the dust figures were on metal, or an enlargement was required, the photograph was taken with a camera, the dust figure being placed in a truly horizontal position, and the camera fixed above with its optical axis vertical. Sometimes, however, a camera enlargement was made from a shadowgraph, as the latter has the advantage of showing the striæ in black lines, whereas the camera photograph shows light and shade on the opposite sides of the ridge.

RESULTS.

Reflexion.—The natural case to test first of all was oblique reflexion from a plane surface. But this failed to exhibit striæ corresponding to any clear distinction between the incident and reflected waves. So, to separate the regions in which incident and reflected waves would occur, an obstacle of plate-glass was used. The corresponding dust figure is reproduced in fig. 1 (Pl. XXI.). Other obstacles were also used so as to form a square with parts of its sides missing, and thus give other examples of reflexion. The striæ at the right-hand upper corner show some distinction between incident and reflected waves. The light diagonal bars at the corners of the square are also noteworthy.

Fig. 2 is a larger example of a square, practically complete. Here again diagonal bars are noticeable, with fainter accompanying bars occupying the whole intermediate spaces. This recalls the effect inside a pentagon obtained by Marsh and Nottage.[1]

Figs. 3 and 4 show triangular dust figures in lycopodium and iron filings respectively. In fig. 3 we have again diagonal bars in the dust figure, but here, the spark being asymmetrical, it is noteworthy that these bars do not tend to meet at the spark but at some other point nearer the centroid of the triangle. In each of the first four figures striæ are seen near the corners *concave to them* (instead of to the spark).

Fig. 4 is one of the very few dust figures obtained fairly well in iron filings. The confinement of the spark disturbance probably assisted the formation. The magnetic field accompanying the discharge was probably a vital factor also in the orientation of the filings. No success attended the endeavour to obtain dust figures with red lead, which is very dense but non-magnetic.

Fig. 5 shows an enlargement from a shadowgraph of the dust figure obtained with an inverted crystallizing dish having a gap at one side next the spark. The reflexion from the interior concave mirror gives a focus distant about half the radius from the centre at the side remote from the spark, as might be expected. But the waves after converging to a focus at half the radius on one side the centre, might diverge again and produce by reflexion a secondary focus at a quarter of the radius on the other side the centre. And this secondary focus, though not anticipated, is clearly shown in the figure. Again, the waves diverging from this could by reflexion form a tertiary focus at a sixth of the radius on the other side the centre, that is, near the primary focus. And this tertiary focus is clearly shown also. Further, these three foci are in diminishing order of distinctness, as might reasonably be expected. It should be observed that the simple distances just referred to are approximate only, being on the supposition that the spark source was at infinity.

Fig. 6 is from an enlarged photograph of one corner of the dust figure confined within a pentagon, the spark being at the centre. This shows very clearly the characteristic corner effect, as though a disturbance were radiating from it after reflexion.

Refraction.—Several attempts were made to obtain refraction effects by letting the disturbance pass from one powder to another very different in density or in some other property. No success was attained in this direction.

But it was noticed that something like refraction occurred near the edge of a cover-plate or any other plate used as a boundary if, instead of fitting close down, a small crevice was left between it and the lower plate. An arrangement was accordingly made on these lines the result of which is shown by the shadowgraph of fig. 7. A piece of glass five inches by one inch with a sloping end was supported on two oblong pieces of card (seen black in the figure) about half a millimetre thick. The refraction of the striæ at the front edge of this plate is clearly exhibited.

Fig. 8 shows a fortuitous example of refraction. It is a photograph of a figure on metal between two inclined boundaries. But the metal was slightly curved, and the boundaries being of plate glass did not fit closely down except near their ends. Consequently, at the sides of the figure remote from the corner a little effect leaked under the glass plates and showed a refraction of the striæ. This figure also shows very clearly the corner effect, for which indeed it was really taken.

Interference.—The simplest way of obtaining interference is that of using two sparks in series. These were passed through holes in the same glass plate, the resulting effect being shown in fig. 9, which is an enlargement of a portion of a shadowgraph. In the dust figure itself (or the print from it), on the part remote from the sparks, the central bar and three on each side of it may be clearly seen. The central bar consists of striæ almost parallel to the line joining the sparks. The second bars to the right or left consist of striæ about perpendicular to those in the central bar. The other four bars or intervening spaces (*i. e.* the first and third on the right and left) do not present striæ, but may be called *cellular* spaces, since the dust is specialized in formation and quite different from the random positions after merely scattering, although no distinct striæ are visible. The above features are considerably modified as the region between the sparks is approached.

But though the above method is the natural one to try first for interference, it is by no means the only one. For, just as in optics and acoustics, interference may be obtained from a single source by reflexion, that should be possible here also. Indeed, cases of it have already occurred. Thus, the diagonal bars near the corners of figs. 1, 2, and 3, and the central bar in fig. 5 are evidently cases of interference or superposition.

But this effect is more strikingly shown in fig. 10 by the central bar in the acute angle between two boundaries, which consisted of glass strips on edge. This case may be contrasted with that of fig. 8, in which leaks occurred at the boundaries and no central bar was formed. The diagonal is well shown also at the acute angle in fig. 11 (Pl. XXII.).

Diffraction.—The effects of spreading out beyond openings or behind obstacles was also sought and obtained. Thus in fig. 11 a very small opening in the boundaries was left at the upper left-hand corner, beyond which the spreading of the striæ is clearly shown. Also beyond the wide opening at the right the spreading is visible, being specially marked near the two corners. It is also noteworthy that in this right-hand portion the striæ are all approximately radial to the spark instead of tangential. This appears to be due to reflexions from the upper and lower boundaries. Thus, the inclined radiation to the upper boundary gives by reflexion an equally inclined radiation from it; and the *resultant* effect of these two is equivalent to motions of the air normally to and from the boundary. Hence the formation of striæ *parallel* to that boundary. And this is the case near the boundary in question. Near the opposite boundary the parallelism of the striæ to it are also noticeable.

The series of effects shown in figs. 12–15 were obtained by placing an obstacle of plate-glass 1 inch square in the inverted crystallizing dish previously used for fig. 5. These were planned with a view to securing a spreading behind the obstacle; and they all give evidence of a running of the disturbance along the edge of the square, thus producing the normal striæ with a radial appearance at the corners.

In each of these four figures (as also in fig. 5) we have portions where the lycopodium is arranged in what may be termed a *cellular* fashion, *i. e.*, it is specialized though not striated. This distinction may be seen at once by contrasting this specialized portion with the random distribution of the scattered and unaffected dust outside the crystallizing dish.

Whispering Gallery.—Scott Russell has pointed out that, in the case of a water-wave proceeding almost parallel to a wall, reflexion fails to occur ; the line of the wave-crest near the wall setting itself normal to the wall, so that the propagation there is along the wall itself. By a similar phenomenon Lord Rayleigh explains the whispering-gallery effect in sound. Again, in the photography of flying bullets, C. V. Boys, in one case, placed an obstacle to find if this sliding instead of reflexion would occur in the breast and tail waves from a bullet. The photograph showed that it did.

It accordingly seemed desirable to ascertain if this whispering-gallery effect could be shown by striations of these dust figures. Fig. 16 shows clearly that it can. The arrangements were of the simplest. A curved card was placed on edge as the boundary, the spark occurred on the concave side near one end of it, and a second card, bent sharply at an angle, was placed to protect the curved boundary from any direct effect of the spark. It is seen that normal striæ about an inch long occur all along the interior of this curved boundary, showing that the air motions are along the boundary itself. At the far end of the figure it is noticeable that the effect partly branches off to the other obstacle.

It is now well to revert to figs. 5, 7, 8, 10, and 12–15. These also show short normal striæ along boundaries curved or straight. These striæ may possibly be produced by a phenomenon analogous to the whispering-gallery effect. Or, perhaps they may be due to the particular phase-difference between the motions of the air at two given points near the boundary. For, on the theory of König [*], where the velocities differ in phase by more than a quarter of a period, there is *attraction* between the spheres at the points in question in cases where, with a phase-difference of less than a quarter of a period, there would be *repulsion* between them. The mechanism of production of some of these normal striæ is accordingly left an open question for the present, but may perhaps repay further investigation.

Fig. 17 may now be noticed. This shows an effect analogous to that of sound passing through a speaking-tube. Two curved cards were used as boundaries in this case. It may be seen that the disturbance passes freely along the curved space between the cards, also that it spreads a little at the far end.

Variation of the Pitch of the Striæ.—To obtain a striking illustration of the variation of the pitch of the striæ under disturbances of different intensities, sinuous boundaries of plate-glass were used. The effect is shown in the enlarged photograph of fig. 18. It is clearly seen that the striæ are coarser in the constrictions where the disturbances are more intense and *vice versa*. A cover-plate was used in producing this figure.

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[*] Wied. *Ann.* xlii. pp. 353, 549 (1891).

It is noteworthy that, in the early progress of the sparking, the striæ appeared at the far end and at the constriction near it, although the intervening wider spaces were up to then quite devoid of striations. As sparking continued, the striations were observed to spread from these constricted portions until the whole figure was striated. Photographs of these early and intermediate stages were taken, but the striations were too fine for easy reproduction.

Fig. 19 shows the effect obtained in iron filings with the same boundaries and cover-plate as for fig. 18. Here the disturbance is so confined that the filings, in spite of their high density, were just sufficiently mobile to allow of a figure being formed.

Successive Sparks.—Although the simultaneous passage of incident and reflected waves over a given region gave striæ in a single direction only, it seemed desirable to try whether crossing striæ were possible by the successive passing of sparks at different places. The effect obtained is shown in the enlarged photograph reproduced in fig. 20. The positions of the two sparks may be inferred from the blown spaces near them and the curvature of the surrounding striæ. This figure is interesting since it shows that when striæ have been formed by one spark, a second spark may be able to produce a second set of striations at an angle with the first, yet without thereby obliterating them. For the two sets of intersecting striæ are clearly visible on the print.

Echelon Reflector.—A step-wise boundary built up of rectangular plate glasses was used to form an echelon to test the possibility of obtaining phenomena analogous to that of the musical echo of a single sudden source. This, however, failed to give any separate evidence of the reflected waves.

Creeping of Striæ in Tubes.—The transverse striæ in tubes were often observed to move bodily along them, usually from the spark, but less frequently towards it. At first the effects presented themselves fortuitously and could not be obtained readily at will. They were afterwards exhibited more plainly and consistently by means of bent tubes. One such tube had two 120° bends, the first and third portions of the tube being about parallel. In each of the three portions of this tube the striæ moved towards the bends. A second tube was used with one right-angle bend. In this tube the striæ beyond the bend moved away from it. But, in the part between the spark and the bend, the striæ divided themselves into two sets side by side, one set moving towards the bend while the other moved towards the spark. This appeared to show that a circulatory motion of the air was occurring in the tube. It was then noticed that such a circulation might be attributed to a side glancing into the tube of the chief energy from the spark which was not quite symmetrically placed at the end of the tube. This asymmetry was then reversed and immediately a reversal of the creeping motions of the striæ was observed.

Inclination of Striæ by Fork.—It seemed of interest to test the effect, if any, on the striæ in a tube, produced by the vibrations of a tuning-fork. A tube $\frac{7}{8}$-inch bore and about 2 feet long was used, the spark being near one end. The other end of the tube was about level with the centre of the mouth of the resonance-box of a fork of frequency 256 per second. When the fork was bowed alone no effect on the dust was perceived. When the sparks passed alone the usual transverse striæ immediately appeared. When, however, the fork was bowed while the sparks were passing, the striæ set themselves at an inclination like the ordinary down-strokes in writing. But when the dust-tube was inserted into the resonance-box so that this open end of the tube was near the closed end of the box, and the experiment repeated, the striæ set themselves at a backward slope.

Other Tests.—Since the striæ appear to be produced by the air-currents in their vicinity, it seemed desirable to use some other gas in place of the air. Thus, in one tube CO_2 was used alternately with air, but the mean of the measurements failed to detect any decided change in the pitch of the striæ.

Magnetic and electric fields were also used on the dust-tubes, but no marked changes in the striæ were thereby produced.

CONCLUSION.

It appears from these experiments that dust figures may be obtained corresponding in their chief features to the ordinary optical phenomena of reflexion, refraction, interference, and diffraction; but that, in addition, the air currents sometimes acquire circulatory or vortex motions, and thus introduce into the dust figures features not present in the optical cases to which they were expected to be analogous.

University College, Nottingham.
July 5th, 1912.

LXXIV. *The Electron Theory of Thermoelectric and Thermionic Effects.* *By* O. W. Richardson, *Professor of Physics, Princeton University*[*].

§ 1. WHAT follows is mainly a discussion of the criticisms by Dr. Bohr[†] and Professor H. A. Wilson[‡], of parts of my recent papers[§]. These criticisms are especially welcome as it is now very desirable, from several points of view, to determine the precise extent and nature of the theoretical warranty which underlies the different formulæ considered. There is probably no more satisfactory method of accomplishing this than by means of an open discussion of the questions at issue. I have also considered the results of some recent experiments by Pring and Parker[||] and Fredenhagen[¶].

§ 2. *Thermoelectric Phenomena.*

The difference between my formulæ and those obtained by Dr. Bohr does not appear to arise from any inherent defect in the method which I employed, but from the fact that I neglected to include effects arising from a possible difference in the rate of transference of kinetic energy by an electric current in different materials. My calculations may easily be extended so as to include these effects in the following manner.

Let us take the Thomson effect first.

The Thomson and Peltier effects are produced by a current flowing uniformly under an applied potential gradient, and, as Dr. Bohr has pointed out, are not necessarily identical with the corresponding effects which are produced by the virtual displacement of an equal number of electrons subject to the equilibrium conditions. In order that we may be sure that σ is really the same thing as the Thomson coefficient, it is necessary to modify a little the cycles such as those considered on p. 603 of my paper. This is to be done in such a way as to make the current flow continuously and reversibly round the cycle, under the influence of an applied electromotive force. The conditions are satisfied if the conductor joining A and A′ is of sufficiently high resistance, and contains a source of electromotive force, if A and A′ are indefinitely large and are contained in chambers bounded by insulating walls covered on the outside by a conducting lining maintained at the potential V′, and if the pistons are sufficiently small and numerous and are made to work fast enough. Since the extra pressure due to the current only introduces second-order terms which vanish in the limit, we are still led to equation (19), except that the meaning of σ and w is different. σ is now equal to the actual specific heat of electricity under the conditions to which it is subject in experimental measurements, and w is the actual internal latent heat of evaporation of the electrons under the condition of continuous flow which holds during the cycle.

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[*] Communicated by the Author.

[†] Phil. Mag. vol. xxiii. p. 984 (1912).

[‡] *Ibid.* vol. xxiv. p. 196 (1912).

[§] *Ibid.* vol. xxiii. pp. 263, 594 (1912).

[||] *Ibid.* vol. xxiii. (1912).

[¶] *Verh. d. Deutsch. Physik. Ges.* 14. Jahrg. p. 384 (1912).

It differs from the corresponding w which occurs in equation (51), p. 619, by an amount which depends on the difference of the rate of transference of kinetic energy by a current on the two sides of the bounding surface. If we keep the symbol w for the w which occurs in equation (20) p. 603, and denote the true static internal latent heat of evaporation which occurs as w in (51), p. 619, by ϕ, then we have the relation

$$w=\phi-(\lambda-\lambda_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ is the energy transferred in unit time by unit electric current in the metal, and λ_0 is the corresponding quantity for the current outside. As before σ is determined by comparison of equations (20) and (51). In this way we arrive at the equivalent expressions:—

$$\sigma=\frac{1}{e}\left\{\frac{R}{\gamma-1}+\theta\frac{\partial}{\partial\theta}\left(\frac{\phi-w}{\theta}\right)-\frac{\partial\phi}{\partial\theta}\right\}, \quad . \quad . \quad . \quad (2)$$

$$=\frac{1}{e}\left\{\frac{R}{\gamma-1}+\frac{w-\phi}{\theta}-\frac{\partial w}{\partial\theta}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$=\frac{1}{e}\left\{\frac{R}{\gamma-1}+\theta\frac{\partial}{\partial\theta}\frac{\lambda_1-\lambda_0}{\theta}-\frac{\partial\phi}{\partial\theta}\right\}, \quad . \quad . \quad . \quad (4)$$

$$=\frac{1}{e}\left\{\frac{R}{\gamma-1}+\theta\frac{\partial}{\partial\theta}\left(\frac{J+\lambda-\lambda_0}{\theta}-R\log K\right)\right\}. \, (5)$$

Quite similar considerations apply in determining the Peltier coefficient. If P is the true value of this, then we obtain the equations:—

$$eP=w_2-w_1-e(V_2-V_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$=\phi_2-\phi_1-(\lambda_2-\lambda_1)-e(V_2-V_1), \quad . \quad (7)$$

$$=J_1-J_2+\lambda_1-\lambda_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

By applying the second law of thermodynamics to a circuit of two metals and substituting the values of P and σ given by (6) and (2), one finds, after integrating by parts,

$$\phi_1-\phi_2=e\left(V_1-V_2-\theta\frac{\partial}{\partial\theta}(V_1-V_2)\right). \quad . \quad . \quad . \quad (9)$$

From the energy equation the thermoelectromotive force may be written in the forms:—

$$T=\frac{1}{e}\int_{\theta_0}^{\theta'}\frac{w_2-w_1+e(V_1-V_2)}{\theta}d\theta, \quad . \quad . \quad . \quad (10)$$

$$=\frac{1}{e}\int_{\theta_0}^{\theta'}\frac{\phi_2-\phi_1-(\lambda_2-\lambda_1)+e(V_1-V_2)}{\theta}d\theta, (11)$$

$$=\Big|V_1-V_2\Big|_{\theta_0}^{\theta'}+\frac{1}{e}\int_{\theta_0}^{\theta'}\frac{w_2-w_1-\phi_2+\phi_1}{\theta}d\theta, (12)$$

$$=\Big|V_1-V_2\Big|_{\theta_0}^{\theta'}+\frac{1}{e}\int_{\theta_0}^{\theta'}\frac{\lambda_1-\lambda_2}{\theta}d\theta. \quad . \quad . \quad (13)$$

The values in terms of J_1 J_2, &c., may be derived by obvious substitutions. The thermoelectric power $\frac{\partial T}{\partial \sigma'}$ is given by differentiating (10)–(13) respectively by the upper limit.

These equations satisfy the conditions $\frac{\partial T}{\partial\theta}=\frac{P}{\theta}$ and $\sigma_1-\sigma_2=\theta\frac{\partial}{\partial\theta}\left(\frac{P}{\theta}\right)$ postulated by Lord Kelvin's theory. They are more general than those given by kinetic theory methods which, it seems to the writer, can only be worked out in rather simple cases which are not likely to exist in nature. They agree with those given by Dr. Bohr when the volume of the regions, within which the forces acting on the electrons are appreciable, is small compared with the volume in which these forces are negligible. This appears to be the most general case which can be treated satisfactorily by the kinetic theory method. The agreement in this case seems strongly to support the validity of the thermodynamic method, and to be subversive of the view that the assumption of reversibility is an arbitrary one.

§ 3. *The Emission of Electrons.*

It is evident that no sound argument can conflict with Professor Wilson's formula :—

$$p=\mathrm{A}\theta^{1+\frac{a}{\mathrm{R}}}e^{-w_0/\mathrm{R}\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which is quite general, subject to the assumed condition that that the true internal latent heat of evaporation is a linear function of θ. This is clearly shown by equation (51) of my paper.

The main use of equation (20) is, therefore, that by comparison with (51) it enables us to deduce a relation between the specific heat of electricity and the temperature variation of the latent heat of evaporation. In virtue of the considerations brought forward in the last section this should be

$$\frac{\partial\phi}{\partial\theta}=\frac{\mathrm{R}}{\gamma-1}+\theta\frac{\partial}{\partial\theta}\left(\frac{\lambda_1-\lambda_0}{\theta}\right)-e\sigma, \quad . \quad . \quad (15)$$

instead of equation (24) of the preceding paper.

There is another point that seems worthy of consideration in this connexion. If N is the number of electrons emitted by a conductor in unit time, n the number in unit volume of the conductor, and w the work they have to do in order to escape, then a calculation based on the kinetic theory shows that

$$\mathrm{N}=n\theta^{\frac{1}{2}}\left(\frac{\mathrm{R}}{2\pi m}\right)^{\frac{1}{2}}e^{-w/\mathrm{R}\theta}. \quad . \quad . \quad . \quad . \quad (16)$$

On the other hand, we have by thermodynamics

$$\mathrm{N}=\mathrm{A}\theta^{\frac{1}{2}}e^{\int\frac{w}{\mathrm{R}\theta^2}d\theta}=\mathrm{A}\theta^{\frac{1}{2}}e^{-\frac{w}{\mathrm{R}\theta}}e^{\int\frac{1}{\mathrm{R}\theta}\frac{\partial w}{\partial\theta}d\theta}, \quad . \quad . \quad (17)$$

where A is independent of θ. Equations (16) and (17) are inconsistent unless

$$n=\text{constant}\times e^{\int\frac{1}{\mathrm{R}\theta}\frac{\partial w}{\partial\theta}d\theta},$$

$$i.\ e.\ \frac{\partial w}{\partial\theta}=\mathrm{R}\theta\frac{\partial}{\partial\theta}(\log n). \quad . \quad . \quad . \quad . \quad (18)$$

Now (16) has only been shown to hold provided the forces to which the electrons are subject are inappreciable except throughout a small proportion of the volume of the conductor. If these or equivalent conditions do not hold, n and w in (16) do not have a precise meaning without further specification.

Subject to these conditions a calculation similar to that given in my paper on the "Theory of Contact Electromotive Force, &c." (Phil. Mag. vol. xxiii. p. 275), but extended so as to take account of a possible difference in the rate of energy transference by the current, shows that

$$\sigma=\frac{1}{e}\left\{\frac{\mathrm{R}}{\gamma-1}+\theta\frac{\partial}{\partial\theta}\left(\frac{\lambda_1-\lambda_0}{\theta}\right)-\mathrm{R}\theta\frac{\partial}{\partial\theta}(\log n)\right\}. \quad (19)$$

From this (18) follows by comparison with (4) above.

It appears, therefore, that (16) and (17) are consistent with one another. If, for example, $w=w_0+a\theta$, it is still true that

$$\mathrm{N}=ne^{-a}\left(\frac{\mathrm{R}}{2\pi m}\right)^{\frac{1}{2}}\theta^{\frac{1}{2}}e^{-w_0/\mathrm{R}\theta}, \quad . \quad . \quad . \quad . \quad (20)$$

$$=\mathrm{A}\theta^{\frac{1}{2}+\frac{a}{\mathrm{R}}}e^{-w_0/\mathrm{R}\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Thus if w ($\equiv\phi$ above) has a temperature coefficient, the determination of n from the temperature variation of the electronic emission would lead to a value which is false by the unknown factor e^{-a}; as I have previously maintained [*]. On the other hand, equation (21), as Professor Wilson pointed out [†], puts a limit on the value of a. In fact, since $\mathrm{N}\propto\theta^{\frac{1}{2}}e^{-b/\theta}$ very nearly, it can be shown that the order of magnitude of a cannot be greater than unity.

The same conclusion is reached by considering equation (15). The various terms on the right when divided by R are of the order unity or less. The term $\theta\frac{\partial}{\partial\theta}\left(\frac{\lambda_1-\lambda_0}{\theta}\right)$ is zero if the force during collisions varies as any power of the mutual distance, and in general there is no reason to expect it to be larger than the other terms. Thus we have every reason for believing that $\frac{1}{\mathrm{R}}\frac{\partial w}{\partial\theta}$ is comparable with unity.

This has an important bearing on the results of some of the experiments which have been made on the emission of electrons by different hot bodies. In my old experiments [‡] with carbon and sodium the currents obtained were much larger than those calculated from the emission from platinum combined with the contact potential differences [*]. As a consequence of this they led to absurdly high estimates of the number of internal free electrons present in these substances [†].

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[*] Phil. Trans. A. vol. cci. p. 543 (1903).

[†] Phil. Trans. A. vol. ccii. p. 260 (1903).

[‡] Phil. Trans. A. vol. cci. p. 497 (1903).

At the time it seemed possible that this discrepancy might be due to the temperature variation of the heat of evaporation being exceptionally large in these cases [‡]; but the above considerations show that such an explanation is insufficient. It is clear that some other cause must be sought for the large effects observed. In the case of carbon, the admixture of more electro-positive substances would provide an adequate explanation, but it is unlikely that a similar explanation would account for the behaviour of an extremely electro-positive substance like sodium. In this case, we have presumably to deal with an effect arising from chemical action.

This position is strengthened by the recent experiments of Pring and Parker [§] on carbon, and of Fredenhagen [||] on sodium and potassium.

The former showed that the currents from carbon could, by purifying the material tested, be reduced to a much smaller value than those which I obtained; whilst Fredenhagen has shown that the currents from the alkali metals are reduced to much smaller values when care is taken to get rid of traces of air or gases which might act chemically on these bodies.

The values of the currents to be expected from sodium are even smaller than those which I originally estimated, owing to the value of w which I used in the case of platinum being too small, as H. A. Wilson showed later [¶]. The value of the currents from platinum, which is given by Wilson, is

$$x=6\cdot 9\times 10^{7}\times \theta^{\frac{1}{2}}\times e^{-\frac{6\cdot 55\times 10^{4}}{\theta}}, \quad . \quad . \quad . \quad (22)$$

where x is the current in amperes per sq. cm. of this substance at θ° K. If we consider an enclosure containing sodium and platinum in thermal equilibrium and in metallic contact at some point, then if ν_{N} is the number of electrons per c.c. at a point outside the sodium, and ν_{P} the corresponding quantity at a point outside the platinum, we see that

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[*] *Cf. loc. cit.* p. 533.

[†] *Loc. cit.* p. 542.

[‡] Phil. Trans. A. vol. cci. p. 544 (1903).

[§] Phil. Mag. vol. xxiii. p. 192 (1912).

[||] *Verh. d. Deutsch. Physik. Ges.* 14. Jahrg. p. 384 (1912).

[¶] Phil. Trans. A. vol. ccii. p. 243 (1903).

$$\nu_{\mathrm{P}}=\nu_{\mathrm{N}}\, e^{-\frac{\mathrm{V}\,.\,ne}{n\mathrm{R}\theta}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where V is the contact potential difference between the two metals, and n is the number of molecules in 1 c.c. of a perfect gas at 0° C. and 760 mm. If we neglect differences in the phenomenon of electron reflexion in the case of the two metals, the saturation currents will be proportional to the corresponding values of ν, so that

$$x_{\mathrm{N}}=x_{\mathrm{P}}\, e^{+\frac{\mathrm{V}\,.\,ne}{n\,.\,\mathrm{R}\theta}}=6{\cdot}9\times 10^{7}\times \theta^{\frac{1}{2}}\times e^{-\frac{6{\cdot}55\times 10^{4}}{\theta}}\times e^{+\frac{\mathrm{V}\,.\,ne}{n\mathrm{R}\,.\,\theta}}\,.\,(24)$$

Consider the case of sodium and potassium at 350° C. In the case of sodium the contact potential difference with platinum is said to be $=2{\cdot}4$ volts. Thus $\mathrm{V}=2{\cdot}4\times 10^{8}$ e.m. units. We also have $\theta=623$, $ne=\cdot 4327$ e.m.u., and $n\mathrm{R}=3{\cdot}72\times 10^{3}$ erg/ °C.

Thus for sodium at 350° C. the expected currents are comparable with

$$x_{\mathrm{N}}=1{\cdot}5\times 10^{-17}\ \mathrm{amp./cm.}^{2}$$

For potassium at the same temperature taking $\mathrm{V}=2{\cdot}7\times 10^{8}$ e.m.u. the expected currents work out at $4{\cdot}3\times 10^{-15}$ amp./cm.^{2} At this temperature the currents from the alkali metals are well below the limits of what can be measured on a galvanometer. If we assume that carbon is 0·3 volt electronegative to platinum, we have for the number of amperes per sq. cm. from this substance at 2000° C., by a similar calculation, the value $x_{\mathrm{C}}=2{\cdot}1\times 10^{-4}$.

It appears, therefore, that the experiments of Pring and Parker, and of Fredenhagen, have removed two outstanding objections to the view that the emission of electrons from pure platinum in a vacuum or in oxygen or nitrogen at a low pressure is independent of chemical action in the ordinary sense.

There are, in my opinion, many other grave objections to such a view. These have been stated elsewhere *, and it would take too much space to recapitulate them here.

I should like to state that I have never been averse to the view that electronic emission may be conditioned by chemical

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* Phil. Trans. A. vol. cci. p. 545 (1903); *ibid.* vol. ccvii. pp. 24, 27, 53, 60 (1906). *Cf.* also H. A. Wilson, "Electrical Properties of Flames, &c.," p. 5 and p. 15; University of London Press, 1912.

action. I have often been surprised that the connexion between the two phenomena is not more general than it appears to be. I do, however, think that there is a considerable body of evidence in favour of the view that there is an emission of electrons from hot conductors which is independent of chemical action.

I ought to add that the experiments of Pring and Parker only support the theory very partially. The currents they obtained at a high temperature are still about 100 times less than those calculated above; but there is sufficient uncertainty in the data to admit the possibility of such a difference without vitiating the theory. The large variation of the current with the pressure of the surrounding gas may be, I think, an immaterial factor, unless the minimum currents can be shown to be too small. The comparative absence of increase of the emission with increasing temperature is a more important consideration and calls for further investigation. Experiments are now being instituted in this laboratory which, I hope, will shed more light on this phenomenon.

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LXXV. *Studies in the Photometry of Lights of Different Colours.—*III. *Distortions in Spectral Luminosity Curves produced by Variations in the Character of the Comparison Standard and of the Surroundings of the Photometric Field.* *By* Herbert E. Ives *.

A PREVIOUS paper in this series described spectral luminosity curves obtained by the equality of brightness and flicker photometers. The mean of the high illumination values as obtained by five observers showed close agreement between the two photometric methods, although the relative positions of the equality of brightness and flicker curves varied among the different individuals. In the same paper attention was drawn to the fact that these measurements covered only a special case, namely, that of comparison of the spectral colours against a single comparison source—the unsaturated yellow of the carbon incandescent lamp. Certain experiments there quoted raised the suspicion that the luminosity curve obtained might be to some extent a function of the colour and saturation of the comparison standard due to the accentuation of colour by simultaneous contrast. As this limitation of conditions also held in the work of Koenig, who used wave-length ·535 μ as his comparison light, and of Abney who used "white," it is a matter of some interest to learn whether this suspicion is upheld or not. The experiments here described give the answer to the question at issue. In addition, another question is investigated, namely, whether an alteration in the surroundings of the photometric field, from dark to light, disturbs one's judgment of equal brightness.

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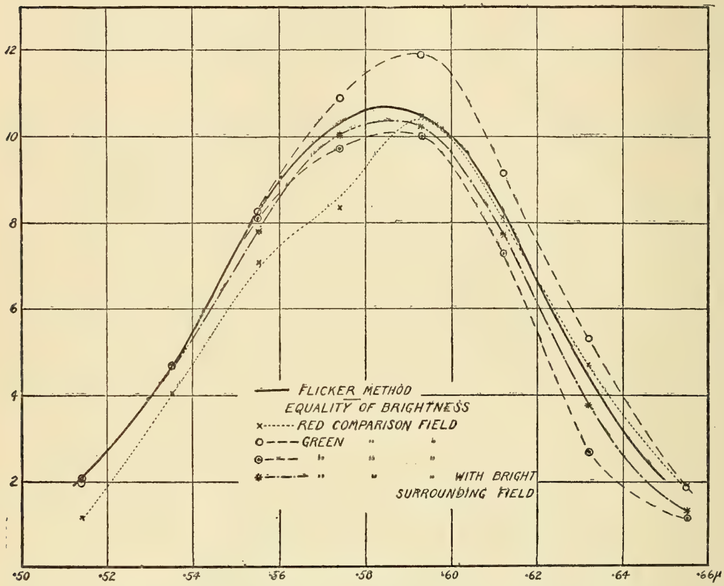
* Communicated by the Author.

In the first of these experiments no change was made in the apparatus as previously described except that red and green glasses were used in connexion with a high intensity (400 cp.) source in order to obtain red, green and "white" comparison illuminations of the same brightness. The red light corresponded in hue to ·62 μ, the green to ·55 μ. With these three colours luminosity curves of the spectrum were made under substantially the conditions of the earlier experiments. Two illuminations were used, a high one of 300 illumination units, a low one of 10 units; two field sizes were used, one of 1°·85 diameter, the other 5° × 8°; the readings were in terms of slit-widths to give equal brightness. The source measured was a normally operated tungsten lamp, as before, but since the results recorded are entirely comparative no values are given for its energy distribution, nor are corrections made for prismatic dispersion.

The results obtained were strikingly different in character by the two photometric methods. By the equality of brightness method a series of different luminosity curves were found, a different one for each colour of comparison standard. These curves vary from each other by amounts as great as would be caused by considerable differences in illumination for a single comparison standard. One of the most significant things about these curves is that no system or regularity has been found in their manner of deviating from "normal." For instance, in fig. 1 (p. 746), where are plotted a set of selected characteristic curves from this series (for high illumination), it will be seen that two made with a green comparison light at different times lie at the two extremes of character. There is not a shift in one direction for a green standard, and in the opposite for a red, but apparently any sort of shift may be expected in changing from one comparison light to another.

It is a common experience in heterochromatic photometry to form a fairly constant criterion of equal brightness when working with a definite set of colours. It is easy to imagine that such a criterion when formed must have some claim to be considered "correct." The previous work of the writer cast doubt on this belief, since the equality of brightness luminosity curves were found to change their shape and position after intervals of time sufficient to destroy one's

Fig. 1.



memory of previous settings. The present work seems to be conclusively against the belief that a "correct" criterion of equal brightness may be attained by mere practice. While with any given comparison source quite definite and consistent spectral luminosity curves may be obtained, these experiments show that after working with several different comparison sources, a return to the first one does not mean a return to the original criterion. It appears therefore that the differences introduced by changing the standard of comparison must be looked upon as psychological. One's judgment is disturbed, and the part played by judgment in the case where different colours are matched for brightness may be very large. The results plotted in fig. 1 are for high illuminations and small field; similar results were obtained for the other conditions of illumination and field size.

These remarks apply only to the equality of brightness method. The curves obtained by the flicker method showed no deviation from each other which could with certainty be considered greater than the errors of measurement. In fig. 1 therefore is plotted a single flicker curve. The equality of brightness curves are grouped about it in a manner to suggest that it is the true normal of which they are all distortions.

The second set of experiments performed was to study the effect of changing the surroundings of the photometric field. It was suggested to the writer by a psychologist that the ordinary optical instrument using a telescope subjects the eye to an abnormal condition in that the field of the instrument is surrounded by a totally black space. Under normal conditions, on the other hand, the whole retina is active. Such an abnormal condition might be expected to disturb such an unstable thing as an equality of brightness judgment.

In order to study this problem the telescope tube of the spectrometer was removed. The eye-slit was attached to a separate rigid stand, the object-glass was held in its original position by a different means. Against the objective were laid large flat metal plates pierced by openings of a size to give the same effective photometric fields as in the previous experiments. These plates were smoked with magnesium oxide and arrangements were made to illuminate them, when in place, by two incandescent lamps whose intensity could be controlled by a series resistance. The plates were of such size that upon turning on the incandescent lamps the whole field of view, except as limited by the ocular slit, was bright. This meant a field of approximately fifty degrees and was considered ample to test the matter in question.

A series of luminosity curves under the same conditions as previously obtained were made, except that both light and dark surroundings were tried. Again the results were in marked contrast as obtained by the equality of brightness and flicker methods. By the former method different curves result depending on the character of the surrounding field. But here, as before, no systematic relationship exists in the curves under the two conditions. The effect of changing the surrounding field from dark to light is to introduce a shift or distortion which may apparently be in either direction. It is again a case of disturbed judgment. In fig. 1 the effect of a light surrounding field as found in one instance is given. With the flicker method, on the other hand, changing the surrounding field introduces no variations certainly larger than the errors of setting.

Before leaving the experiments on light and dark surroundings some incidental results may be noted. With the small field, using the equality of brightness method, a very considerable increase in definiteness of setting was found with the bright surrounding field. A similar increase was not found with the large field, nor by the flicker method, but in the latter a bright surrounding field necessitated a higher speed for the rotating disk. Although no certain increase in sensibility appeared, considerably greater comfort was felt in working with the larger area of retina active, which would recommend that condition for accurate work if a small field is used.

At low illuminations with a large field where the Purkinje effect appears in the equality of brightness method, and the opposite effect by the flicker method, an interesting question is whether these effects are to be connected with the excitation of a large retinal area or only with the area which is concerned with the actual comparisons of brightness, or detection of flicker. In short, at low illuminations, will surrounding a small photometric field with a large bright area be equivalent to using a large photometric field? The answer is in the negative, for while bright surroundings shift the equality of brightness curves, the shifts are neither in direction or amount consistently such as would be called Purkinje shifts, and with the flicker method the absence of any shift disposes of the question at once.

It is evident from these experiments that no reliance may be placed upon an equality of brightness luminosity curve obtained under such conditions that the psychological element of the judgment of equality of essential inequalities is necessary. The fact that the flicker photometer is free from such uncertainty is a strong argument in its favour. There still remains unsettled, however, the question whether the flicker photometer gives something that may with propriety be called the true brightness. In other words, does it give what would be obtained by the equality of brightness method with the psychological variables eliminated?

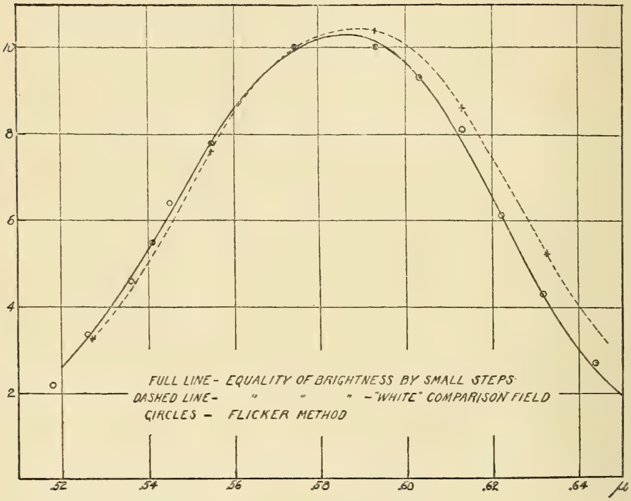
This query naturally leads to the consideration of a method of heterochromatic photometry which has been advocated and used in certain cases, namely that by steps of small hue difference, or in cascade, as it is sometimes called. The principle is that if the hue difference is made small enough it will not disturb the brightness judgment. In establishing incandescent lamp photometric standards of different colour, this method is particularly feasible, since all intermediate colours are obtainable by voltage variation.

In order to obtain spectral luminosity curves by this method, two additions were made to the apparatus as previously described. First a second spectrometer similar to the first, but with its telescope removed, was added. A first surface platinum mirror, obtained by cathode deposition on a piece of glass, which was afterward cut in two to make a sharp edge, was placed directly behind and parallel to the rotating disk, and so arranged that it could be drawn up out of place. The second spectrometer was then so placed that the light from its prism was received by the mirror and reflected into the telescope of the original instrument. In this way half the field received light from each instrument, and any two spectral colours could be compared by the equality of brightness method. The flicker disk and comparison lamp being undisturbed, it was possible at any time to secure a flicker photometer curve. As these were proved to be independent of the kind of comparison lamp used, it was not necessary to arrange to secure such curves for different spectral comparison colours, as might at first sight have been thought necessary for completeness.

These experiments were carried out only at the high illumination for the small field size, and with a bright surrounding field, these being the conditions dictated by all the work up to the present as best for accuracy and freedom from disturbances of all sorts, and so best fitted to be established as standard. Starting at the middle of the spectrum, the two sides of the field were made alike in hue and closely the same in brightness, and their relative brightness measured, then one side was changed to a wave-length only slightly removed and its brightness was measured, the wave-length difference being such as to introduce only a very slight hue difference. The comparison field was again made like the test side, the latter moved to a new wave-length and the brightness of this step compared with the first, and so on through the spectrum. Then starting at either end with the slit-width values obtained by working from the centre, the spectrum was measured continuously to the other end.

The curves obtained by this procedure were unsatisfactory, because of cumulative errors. Upon returning from red to blue, after working from blue to red, the original value for the end of the spectrum was not obtained. In order to eliminate all possibility of systematic drift such as might be caused by favouring the new hue, or one side of the photometer field, the following scheme was substituted for the first :—At numerous points in the spectrum, at the approximate slit-widths found from the mean of the previous work as necessary for equal brightness, the ratio of brightness of λ to $\lambda-\Delta\lambda$ was measured. For $\Delta\lambda$ was chosen $\cdot004\,\mu$, which means everywhere a very small hue difference. The measurements were made at points taken absolutely haphazard, and each measurement consisted of four, first with both sides of the field illuminated by λ : second, the right-hand side by λ, the left by $\lambda-\Delta\lambda$; third, both sides by $\lambda-\Delta\lambda$; fourth, the right-hand side by $\lambda-\Delta\lambda$, the left by λ. From these two values of the ratio $\frac{\lambda}{\lambda-\Delta\lambda}$ were obtained and their mean was adopted. These values were plotted as a curve, and from this was built up the luminosity curve shown in fig. 2,

Fig. 2.



a curve which may fairly be claimed to be independent of the psychological errors illustrated by fig. 1.

After obtaining this luminosity curve, a flicker curve and an equality of brightness curve, by the ordinary method, against incandescent lamp light, were made. These are shown as well in fig. 2. It will be seen that the flicker curve (circles) agrees with the special small step equality of brightness one. The ordinary equality of brightness curve happens to be quite different from the flicker curve.

This result is in agreement with the conclusion drawn from the previous work with five observers, that when the psychological errors are eliminated the equality of brightness and the flicker photometers agree at high illuminations. In the one case an attempt was made to eliminate the psychological difficulty by taking the mean of several different observers, in the second case by a special method of observation. In the writer's opinion these results justify the opinion that the flicker photometer gives, under the conditions specified, what may be considered the true brightness.

It follows from this work that previously obtained spectral luminosity curves, such as those of Kœnig and Abney where the equality of brightness method was used, are subject to considerable uncertainties. While in the case of Kœnig's curves for different illuminations the amount and direction of the changes constituting the Purkinje effect may be substantially correct, the absolute values for the energy-luminosity values cannot be considered as sufficiently exact to be taken as normal. In view of the results of this paper it is probable that the mean flicker curve given in the first paper of the series is more entitled to be called a normal luminosity curve than any previously obtained ones.

The main results of this paper may be summarized as follows:—

1. With the equality of brightness method the effect of changing the colour of the comparison field and of substituting light for dark surroundings to the photometric field is to introduce irregular and unsystematic shifts and distortions of the spectral luminosity curves.

2. With the flicker method, the corresponding changes produce no alterations in the luminosity curves.

3. The equality of brightness spectral luminosity curve obtained by taking small steps of slight hue difference, agrees at high illuminations, for a small field, with the curve given by the flicker photometer.

4. It is concluded that the flicker photometer gives, under the specified conditions, the true brightness.

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May, 1912.

LXXVI. *On some Iridescent Films.*

By Lord Rayleigh, *O.M.*, *F.R.S.*[*]

THE experiments now to be described originated in an accidental observation. Some old lantern-plates, from which the gelatine films had been cleaned off a few years before (probably with nitric acid), being required for use, were again placed in dilute nitric acid to ensure cleanliness. From these plates a gas-flame burning over the dish was seen reflected with colour, of which the cause was not obvious. On examination in daylight a dry plate was observed to be iridescent, but so slightly that the fact might easily escape attention. But when the plate was under water and suitably illuminated, the brilliancy was remarkably enhanced. Upon this question of illumination almost everything depends. The window-shutter of one of the rooms in my laboratory has an aperture about 4 inches square. In front of this the dish of water is placed and at the bottom of the dish a piece of dark-coloured glass. In the water the plate under observation is *tilted*, so as to separate the reflexions of the sky as given by the plate and by the glass underneath. In this way a dark background is ensured. At the corners and edges of the plate the reflected light is white, then follow dark bands, and afterwards the colours which suggest reflexion from a thin plate. On this view it is necessary to suppose that the iridescent film is thinnest at the outside and thickens towards the interior, and further, that the material constituting the film has an index intermediate between those of the glass and of the water. In this way the general behaviour is readily explained, the fact that the colours are so feeble in air being attributed to the smallness of the optical difference between the film and the glass underneath. In the water there would be a better approach to equality between the reflexions at the outer and inner surfaces of the film.

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[*] Communicated by the Author. Read before the British Association at Dundee.

From the first I formed the opinion that the films were due to the use of a silicate substratum in the original preparation, but as the history of the plates was unknown this conjecture could not be satisfactorily confirmed. No ordinary cleaning or wiping had any effect; to remove the films recourse must be had to hydrofluoric acid, or to a polishing operation. My friend Prof. T. W. Richards, after treating one with strong acids and other chemicals, pronounced it to be what chemists would call "very insoluble." The plates first encountered manifested (in the air) a brilliant glassy surface, but afterwards I found others showing in the water nearly or quite as good colours, but in the air presenting a smoky appearance.

Desirous of obtaining the colours as perfectly as possible, I endeavoured to destroy the reflexion from the back surface of the plate, which would, I supposed, dilute the colours due to the iridescent film. But a coating of black sealing-wax, or marine glue, did not do so much good as had been expected. The most efficient procedure was to grind the back of the plate, as is very easily done with carborundum. The colours seemed now to be as good as such colours can ever be, the black also being well developed. Doubtless the success was due in great measure to the special localized character of the illumination. The substitution of strong brine for water made no perceptible improvement.

At this stage I found a difficulty in understanding fully the behaviour of the unground plates. In some places the black would occasionally be good, while in others it had a washed-out appearance, a difference not easily accounted for. A difficulty had already been experienced in deciding upon which side of a plate the film was, and had been attributed to the extreme thinness of the plates. But a suspicion now arose that there were films upon *both* sides, and this was soon confirmed. The best proof was afforded by grinding away half the area upon one side of the plate and the other half of the area upon the other side. Whichever face was uppermost, the unground half witnessed the presence of a film by brilliant colouration.

Attempts to produce silicate films on new glass were for some time an almost complete failure. I used the formula given by Abney (Instruction in Photography, 11th edition, p. 342):—

Albumen	1 part.
Water	20 parts.
Silicate of Soda solution of syrupy consistency	1 part.

But whether the plates (coated upon one side) were allowed to drain and dry in the cold, or were more quickly dried off over a spirit flame or before a fire, the resulting films washed away under the tap with the slightest friction or even with no friction at all. Occasionally, however, more adherent patches were observed, which could not so easily be cleaned off. Although it did not seem probable that the photographic film proper played any part, I tried without success a superposed coat of gelatine. In view of these failures I could only suppose that the formation of a permanent film was the work of time, and some chemical friends were of the same opinion. Accordingly a number of plates were prepared and set aside duly labelled.

Examination at intervals proved that time acted but slowly. After six months the films seemed more stable, but nothing was obtained comparable with the old iridescent plates. It is possible that the desired result might eventually be achieved in this way, but the prospect of experimenting under such conditions is not alluring. Luckily an accidental observation came to my aid. In order to prevent the precipitation of lime in the observing-dish a few drops of nitric acid were sometimes added to the water, and I fancied that films tested in this acidified water showed an advantage. A special experiment confirmed the idea. Two plates, coated similarly with silicate and dried a few hours before, were immersed, one in ordinary tap water, the other in the same water moderately acidified with nitric acid. After some 24 hours soaking the first film washed off easily, but the second had much greater fixity. There was now no difficulty in preparing films capable of showing as good colours as those of the old plates. The best procedure seems to be to dry off the plates before a fire after coating with recently-filtered silicate solution. In order to obtain the most suitable thickness, it is necessary to accommodate the rapidity of drying to the strength of the solution. If heat is not employed the strength of the above given solution may be doubled. When dry the plates may be immersed for some hours in (much) diluted nitric acid. They are then fit for optical examination, but are best not rubbed at this stage. If the colours are suitable the plates may now be washed and allowed to dry. The full development of the colour effects requires that the back of the plates be treated. In my experience grinding gives the best results when the lighting is favourable, but an opaque varnish may also be used with good effect. The comparative failure of such a treatment of the old plates was due to the existence of films upon both sides. A sufficiently opaque glass, *e.g.* stained with cobalt or copper, may also be employed. After the films have stood some time subsequently to the treatment with acid, they may be rubbed vigorously with a cloth even while wet; but one or two, which probably had been rubbed prematurely, showed scratches.

The surfaces of the new films are not quite as glassy as the best of the old ones, nor so inconspicuous in the air, but there is, I suppose, no doubt that they are all composed of silica. But I am puzzled to understand how the old plates were manipulated. The films cover both sides without interruption, and are thinner at all the four corners than in the interior.

The extraordinary development of the colours in water as compared with what can be seen in air led me to examine in the same way other thin films deposited on glass. A thin coat of albumen (without silicate) is inconspicuous in air. As in photography it may be rendered insoluble by nitrate of silver acidified with acetic acid, and then exhibits good colours when examined under water with favourable illumination. Filtered gelatine, with which a little bichromate has been mixed beforehand, may also be employed. In this case the dry film should be well exposed to light before washing. Ready-made varnishes also answer well provided they are capable of withstanding the action of water, at least for a time. I have used amber in chloroform, a "crystal" (benzole) varnish such as is, or was, used by photographers, and bitumen dissolved in benzole. The last is soon disintegrated under water, but the crystal varnish gives very good films. The varnish as sold may probably require dilution in order that the film may be thin enough.

Another varnish which gives interesting results is celluloid in pear-oil. All these films show little in air, but display beautiful colours in water when the reflexion from the back of the glass is got rid of as already described. The advantage from the water depends, of course, upon its mitigating the inequality of the reflexion from the two sides of the film by diminishing the front reflexion. A similar result may be arrived at by another road if we can increase the back reflexion, with the further advantage of enhanced illumination. For this purpose we may use silvering. A glass is coated with a very thin silver film and then with celluloid varnish of suitable consistency Magnificent colours are then seen without the aid of water, and the only difficulty is to hit off the right thickness for the silver. Other methods of obtaining similar displays are described in Wood's 'Physical Optics' (MacMillan, 1905, p. 142).

LXXVII. *On the Bending of Electric Waves round a Large Sphere.*—V. *By* J. W. Nicholson, *M.A., D.Sc.*[*]

Points near the axis in the region of brightness.

We can now show that the second approximation obtained in the preceding section [†] for points in the region of brightness does not fail near the axis, and, in fact, we can derive the solution for this entire region without the use of an approximate formula for the zonal harmonic. A brief account of this investigation is now given, as most of the necessary analysis has already appeared in the section immediately preceding, the main difference being dependent on the mode of treatment of $P_n(\mu)$. If the accurate Mehler Dirichlet integral is used for this function, the magnetic

[*] Communicated by the Author.

[†] Phil. Mag. Mar. 1911, p. 281.

force is given as in (112) by

$$\gamma p = g(\theta)\Sigma_1^\infty u(e^{\iota v_1}+e^{\iota v_2}),$$

where

$$u=\tfrac{1}{2}m(\mathrm{R}_n\mathrm{R}_{nr})^{\frac{1}{2}}(1+e^{2\iota\chi_n}), \quad (v_1, v_2)=\phi_n-\phi_{nr}\pm m\phi, \quad . \quad (158)$$

and

$$g(\theta)\omega=\frac{2\iota\sin^2\theta}{ka^2\pi}\frac{d}{d\mu}\int_0^\theta\frac{\omega\,d\phi}{\sqrt{2}\sqrt{\cos\phi-\cos\theta}},$$

and where the series with exponent v_1 may be neglected, to the order concerned, because the derivate of this exponent cannot vanish. The derivate of the other exponent vanishes where

$$x=\sin\phi/(1-2c\cos\phi+c^2)^{\frac{1}{2}}, \quad c=a/r.$$

We shall restrict attention at once to the effect at some distance from the sphere, so that c is zero, and the zero point is $x=\sin\phi$. The reduction of the formulæ is simple, by virtue of the theorem given in (138), that the sum of a series

$$\Sigma=\Sigma_0^\infty ue^{\iota zv} \quad . \quad . \quad . \quad . \quad . \quad . \quad (159)$$

with the usual notation of this paper, is, under certain conditions already shown to be satisfied, given to a second approximation by

$$\Sigma=\left(\frac{2\pi z}{v_2}\right)^{\frac{1}{2}}\left\{u+\frac{\iota\mu}{2z}\right\}e^{\iota zv+\frac{1}{4}\iota\pi}, \quad . \quad . \quad (160)$$

the values being taken at the zero point, and suffixes denoting differentiations with respect to x or $(n+\frac{1}{2})/z$. The magnitude μ is given by

$$\mu=\frac{u_2}{v_2}-\frac{u_1v_3}{v_2^2}-\frac{1}{4}\frac{uv_4}{v_2^2}+\frac{5}{12}\frac{uv_3^2}{v_2^3}. \quad . \quad . \quad (161)$$

In the neighbourhood of the zero point, ϕ_n and ϕ_{nr} become as usual, the latter relating to a large value of r,

$$\left.\begin{aligned}\phi_n&=\frac{\pi}{4}+z\left\{\sqrt{1-x^2}+x\sin^{-1}x-\frac{\pi x}{2}\right\}\\ \phi_{nr}&=\frac{\pi}{4}+kr-\frac{\pi zx}{2}\end{aligned}\right\} \quad . \quad . \quad (162)$$

These are the first approximations. As in (147), we may continue to use these in finding a second order solution providing that u is multiplied by

$$1+\frac{\iota}{8z}\left\{\frac{1}{(1-x^2)^{\frac{1}{2}}}-\frac{c}{(1-c^2x^2)^{\frac{1}{2}}}+\frac{5}{3}\frac{x^2}{(1-x^2)^{\frac{3}{2}}}-\frac{5}{3}\frac{c^2x^2}{(1-c^2x^2)^{\frac{3}{2}}}\right\},$$

or, in the present case of a large distance from the sphere, by

$$1+\frac{\iota}{8z}\left\{\frac{1}{(1-x^2)^{\frac{1}{2}}}+\frac{5}{3}\frac{x^2}{(1-x^2)^{\frac{3}{2}}}\right\}. \quad . \quad . \quad (163)$$

As before, $1+e^{2\iota\chi_n}$ becomes $2+\iota x^2/z(1-x^2)^{\frac{3}{2}}$, and with these values, and

$$R_n=(1-x^2)^{-\frac{1}{2}}, \quad R_{nr}=1,$$

we find for the problem in hand,

$$u=\frac{zx}{(1-x^2)^{\frac{1}{4}}}\left(1+\frac{\iota\lambda}{z}\right),$$

$$zv=z\{\sqrt{1-x^2}+x\sin^{-1}x\}-kr+zx\phi,$$

where

$$\lambda=\frac{x^2}{2}(1-x^2)^{-\frac{3}{2}}+\frac{1}{8}(1-x^2)^{-\frac{1}{2}}+\frac{5}{24}(1-x^2)^{-\frac{3}{2}}. \quad (164)$$

Differentiating, we have *first* approximations to u_1 and u_2 in the forms

$$u_1=\tfrac{1}{2}(2-x^2)(1-x^2)^{-\frac{5}{4}},$$

$$u_2=\tfrac{1}{4}zx(6-x^2)(1-x^2)^{-\frac{9}{4}}.$$

These are, as before, not required to the second order. Let $C=\cos\phi$, and $S=\sin\phi$. Then at the zero point, u being its first approximation,

$$u_1/u=(2-S^2)/2SC^2,$$

$$u_2/u=(6-S^2)/4C^4,$$

$$\lambda=(3+14S^2)/24C^3,$$

$$v_2=1/C, \quad v_3=S/C^3, \quad v_4=(1+2S^2)/C^5,$$

the values of the v's being quoted from (152) with ϕ written for θ.

Thus, on reduction,

$$\frac{\mu}{u}=-\frac{1}{4}\left(\frac{v_4}{{v_2}^2}-\frac{5}{3}\frac{{v_3}^2}{{v_2}^3}\right)-\frac{v_3}{{v_2}^2}\frac{u_1}{u}+\frac{1}{v_2}\frac{u_2}{u}=(3+2S^2)/12C^3. \quad (165)$$

The first approximation to u is $z\mathrm{S}/\mathrm{C}^{\frac{1}{2}}$, and in terms of this approximation, by (160) and (164),

$$\Sigma=\left(\frac{2\pi z}{v_2}\right)^{\frac{1}{2}}u\left(1+\frac{\iota\delta}{z}\right)e^{\iota z v_0+\frac{1}{4}\iota\pi},$$

where $\delta=\lambda+\frac{1}{2}\mu/u$, so that finally, v_0 being $z\cos\phi-kr$,

$$\Sigma=\sqrt{2\pi z^3}\,\mathrm{S}\left(1+\frac{\iota\delta}{z}\right)e^{\iota\frac{\pi}{4}-\iota kr+\iota z\mathrm{C}},$$

where

$$\delta=(3+8\mathrm{S}^2)/12\mathrm{C}^3, \quad . \quad . \quad . \quad . \quad . \quad (166)$$

and δ is of the same form as before, with ϕ for θ.

The magnetic force is therefore given by

$$\begin{aligned}\gamma\rho&=g(\theta)\Sigma\\&=-\frac{2\iota\sin\theta}{ka^2\pi}\frac{d}{d\theta}\int_0^\theta\frac{\Sigma d\phi}{\sqrt{2}\sqrt{\cos\phi-\cos\theta}}\\&=\frac{2k\sin\theta}{\sqrt{\pi ka}}\cdot e^{-\iota kr-\frac{1}{4}\iota\pi}\frac{d}{d\theta}\int_0^\theta\frac{d\phi\sin\phi}{\sqrt{\cos\phi-\cos\theta}}\left(1+\frac{\iota(3+8\sin^2\phi)}{12ka\cos^3\phi}\right)e^{-\iota ka\cos\phi}\end{aligned}$$

$$. \quad . \quad . \quad (167)$$

Now if I_1 is the integral,

$$\mathrm{I}_1=\int_0^\theta\frac{d\phi\sin\phi}{\sqrt{\cos\phi-\cos\theta}}e^{\iota ka\cos\phi}. \quad . \quad . \quad (168)$$

Then with $\cos\phi=\cos\theta+w^2$,

$$\mathrm{I}_1=2e^{\iota ka\cos\theta}\int_0^{2^{\frac{1}{2}}\sin\frac{1}{2}\theta}dw\,e^{\iota kaw^2},$$

and

$$\frac{d\mathrm{I}_1}{d\theta}=-2ika\sin\theta\,e^{ika\cos\theta}\int_0^{2^{\frac{1}{2}}\sin\frac{1}{2}\theta}dw\,e^{\iota kaw^2}+2^{\frac{1}{2}}\cos\tfrac{1}{2}\theta e^{\iota z},$$

the second term arising from differentiation of the limit of integration.

But to a *second* approximation, by the usual formula for an integral of Fresnel's type,

$$\int_0^{2^{\frac{1}{2}}\sin\frac{1}{2}\theta}dw\,e^{\iota ka w^2}=\frac{1}{2}\left(\frac{\pi}{ka}\right)^{\frac{1}{2}}e^{\frac{1}{4}\iota\pi}+\frac{e^{\iota z(1-\cos\theta)}}{2\sqrt{2}\iota z\sin\frac{1}{2}\theta}, \quad (169)$$

if $z\sin\frac{1}{2}\theta$ is not small. On substitution of this value, the second term of $d\mathrm{I}_1/d\theta$ is removed, and to the *second* order of $(ka)^{-1}$,

$$\frac{d\mathrm{I}_1}{d\theta}=-\iota(\pi ka)^{\frac{1}{2}}\sin\theta\,e^{\iota ka\cos\theta+\frac{\iota\pi}{4}}. \quad . \quad . \quad (170)$$

A first order value only of the second integral,

$$I_2=\int_0^\theta \frac{d\phi \sin\phi}{\sqrt{\cos\phi-\cos\theta}} \cdot \frac{3+8\sin^2\phi}{\cos^3\phi} e^{\iota ka\cos\phi} \qquad (171)$$

is required. The important part of this integral is contributed at the upper limit, and is given by

$$I_2=\frac{3+8\sin^2\theta}{\cos^3\theta}\int_0^\theta \frac{d\phi\sin\phi}{\sqrt{\cos\phi-\cos\theta}} e^{\iota ka\cos\phi},$$

or

$$I_2=\left(\frac{\pi}{ka}\right)^{\frac{1}{2}}\frac{3+8\sin^2\theta}{\cos^3\theta} \cdot e^{\iota ka\cos\theta+\frac{1}{4}\iota\pi},$$

and to the same order,

$$\frac{dI_2}{d\theta}=-\iota(\pi ka)^{\frac{1}{2}}\frac{\sin\theta}{\cos^3\theta}(3+8\sin^2\theta)e^{\iota ka\cos\theta+\frac{1}{4}\iota\pi}, \qquad (172)$$

so that to a second approximation, with a relative order $(z\theta)^{-1}$,

$$\gamma\rho=\frac{2k\sin\theta}{\sqrt{\pi ka}}e^{-\iota kr-\frac{1}{4}\iota\pi}\left(\frac{dI_1}{d\theta}+\frac{\iota}{12ka}\frac{dI_2}{d\theta}\right),$$

$$=-2\iota k\sin^2\theta\left(1+\frac{\iota\delta}{ka}\right)e^{-\iota kr+\iota ka\cos\theta},$$

where

$$\delta=(3+8\sin^2\theta)/12\cos^3\theta. \quad . \quad . \quad . \qquad (173)$$

This is identical with (155), and has been shown to be valid so long as $z\sin\frac{1}{2}\theta$ or $\frac{1}{2}z\theta$ is small. If z is 10^6 as in our usual numerical case, $z\theta=10$ if θ is about two seconds. In other words, the result is valid actually on the axis, and the solution does not change in type near that axis, in accordance with the statement at the end of the preceding section. The actual effect is practically evanescent at such a small orientation.

General investigation of the Shadow.

The only remaining case which demands solution is that of the intensity at any point in the shadow, and to this we proceed. The intensity for any point on the surface of the sphere has been tabulated already, and the results for any other point in the shadow may be derived very readily, after the same manner, from preceding analysis. The problem thus contemplated includes, of course, that of a raised receiver of the waves.

We recall from (83) that the magnetic force in the shadow is given by

$$\gamma\rho = \mathrm{G}(\theta)\sum_{n=1}^{\infty} m(\mathrm{R}_n\mathrm{R}_{nr})^{\frac{1}{2}}(1+e^{2\iota\chi_n})\sin m\phi\, e^{\iota(\phi_n-\phi_{nr})}, \quad (174)$$

where $\mathrm{G}(\theta)$ is an operation similar to $g(\theta)$, and defined by

$$\mathrm{G}(\theta)\,\omega = \frac{2\iota\sin^2\theta}{ka^2\pi}\frac{d}{d\theta}\int_{\theta}^{\pi}\frac{\omega\, d\phi}{\sqrt{2}\,\sqrt{\cos\theta-\cos\phi}} \qquad (175)$$

and the exponents of the component series of $\gamma\rho$ have no zero points. Since the integral formula for the zonal harmonic is used, the result will not fail on the axis of the shadow.

It was also shown, as in (89) and afterwards, that when expressed as a function of m or $n+\frac{1}{2}$, the function $m\mathrm{R}_n(1+e^{2\iota\chi_n})$ is an *odd* function, and the conclusion was derived that when $\mathrm{R}_{nr}=\mathrm{R}_n$ and $\phi_{nr}=\phi_n$, the harmonics of low order in the series (174) cannot give a special contribution of non-exponential type to $\gamma\rho$, but must be included in the sum subsequently derived by a use of Cauchy's theorem of residues.

The process of summation adopted would not, in general, be useful in the presence of an exponent of argument $\phi_n-\phi_{nr}$ which oscillates. We proceed to consider the present problem by the same method, adjusting the analysis where necessary.

In the first place, as in (89), R_{nr} is given by

$$\mathrm{R}_{nr} = \frac{4kr}{\pi}\int_0^{\infty}\mathrm{K}_0(2kr\sinh t)\cosh 2mt\, dt, \quad . \quad (176)$$

and this is an even function of m. The functions ϕ_n and ϕ_{nr} are not even in m, as may be seen, for example, by an inspection of one of the forms of ϕ_n, namely,

$$\phi_n = \sqrt{z^2-m^2} - m\sin^{-1} m/z - m\pi/2 + \pi/4.$$

But $\phi_n-\phi_{nr}$ may be shown to be an even function. For in general *,

$$\left.\begin{aligned}\phi_n &= -\int_z^{\infty}\left(\frac{1}{\mathrm{R}_n}-1\right)dr + z - \tfrac{1}{2}m\pi - \tfrac{1}{4}\pi\\ \phi_{nr} &= -\int_r^{\infty}\left(\frac{1}{\mathrm{R}_{nr}}-1\right)k\,dr + kr - \tfrac{1}{2}m\pi - \tfrac{1}{4}\pi\end{aligned}\right\} \quad (177)$$

where both R_n and R_{nr} are even functions of m. Thus $\phi_n-\phi_{nr}$ is at once seen to be an even function of m also.

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* "The Asymptotic Expansions of Bessel Functions," Phil. Mag. Feb. 1910, p. 235.

Let $m=\nu$ be a typical singularity of the function

$$\tfrac{1}{2}\iota(\mathrm{R}_n\mathrm{R}_{nr})^{\frac{1}{2}}(1+e^{2\iota\chi_n})e^{\iota(\phi_n-\phi_{nr})} \quad . \quad . \quad . \quad (178)$$

in the plane of the variable m, now complex. All such singularities must be simple poles, for $\phi_n-\phi_{nr}$ has no infinities, since R_n and R_{nr}, by their expressions as definite integrals, have no zeros (for finite values of m), and in other respects the function does not differ from its old value for points on the surface of the sphere. This value, as we showed, only led to simple poles.

Since the function is even, $m=-\nu$ is also a pole, and if a_ν is the residue of the function at $m=\nu$, the corresponding part of its development by Cauchy's theorem is

$$a_\nu\left(\frac{1}{m-\nu}-\frac{1}{m+\nu}\right)=\frac{2\nu a_\nu}{m^2-\nu^2}.$$

Thus the value of $\gamma\rho$ is

$$\gamma\rho=\mathrm{G}(\theta)\sum_{n=1}^{\infty}m(\mathrm{R}_n\mathrm{R}_{nr})^{\frac{1}{2}}(1+e^{2\iota\chi_n})\sin m\phi\, e^{\iota(\phi_n-\phi^{nr})}$$

$$=-\iota\mathrm{G}(\theta)\,\Sigma_\nu\, 2\nu a_\nu \sum_{m=-\infty}^{m=\infty}\frac{m\sin m\phi}{m^2-\nu^2} \quad . \quad . \quad . \quad . \quad (179)$$

as in (95), with the new meaning of a_ν, m taking half integral values in the last summation, which may be effected as before.

The first pole is again given by

$$m=z-\iota z^{\frac{1}{3}}\beta,$$

and will be found to be the only important one. As in (97), we find ultimately

$$\gamma\rho=-\frac{2\sin\theta}{ka^2}(2\pi\sin\theta)^{\frac{1}{2}}\,\Sigma_\nu\,\nu^{\frac{3}{2}}a_\nu e^{-\iota\nu\theta+\frac{1}{4}\iota\pi} \quad . \quad (180)$$

at a point whose orientation is θ.

Now for points on the surface, the value of a_ν is $z^{\frac{2}{3}}/2\iota\beta$ as in (98), where β corresponds to ν, so that $\nu_r=z-\iota z^{\frac{1}{3}}\beta_r$ defines the rth pole, and if the order r of the singularity is unity, $\beta=\cdot696$, as in (107). The residues are not of an oscillatory type in this case. But in the present problem, a is the residue of a function whose exponent oscillates, so that a_ν can oscillate in passing from one singularity to another. If, therefore, this exponent should possess a zero point, or a minimum point as defined in the section dealing with the transitional region, the sum of the series (180) would not be given effectively by its first term. Successive terms would not decrease exponentially, and a process of summation would be required for this series. This would involve difficulties.

But we have shown the absence of such zero points within the shadow, and therefore the absence of this special difficulty. It is now evident that in the present problem, a determination of a_ν for the first singularity will complete the physical solution. But it is also evident that a similar treatment would fail for points not inside the geometrical shadow.

The determination of a_ν may be made at once. For it will differ from its value for points on the surface, only by a factor

$$(\mathrm{R}_{nr}/\mathrm{R}_n)^{\frac{1}{2}} e^{\iota(\phi_n - \phi_{nr})}, \quad . \quad . \quad . \quad . \quad (181)$$

provided that we substitute, in this factor, the value of m given by

$$m = z - \iota z^{\frac{1}{3}} \beta,$$

where β has its previous value ·696.

Consider now a point in the shadow at distance r from the centre, and at such a distance from the surface that $kr - z$ is of higher order than $z^{\frac{1}{3}}$. Then

$$kr - m = kr - z + \iota z^{\frac{1}{3}} \beta$$

is also of higher order than $z^{\frac{1}{3}}$, and its real part is positive. Accordingly, selecting the appropriate asymptotic expansions,

$$\left.\begin{aligned} \mathrm{R}_{nr} &= kr/(k^2r^2 - m^2)^{\frac{1}{2}} \\ \phi_{nr} &= (k^2r^2 - m^2)^{\frac{1}{2}} + m \sin^{-1} m/kr - \tfrac{1}{2} m\pi + \tfrac{1}{4}\pi. \end{aligned}\right\} \quad (182)$$

Thus, with $m = z - \iota z^{\frac{1}{3}}\beta$, the significant values become

$$\mathrm{R}_{nr} = kr/(k^2r^2 - z^2)^{\frac{1}{2}} = (1 - a^2/r^2)^{-\frac{1}{2}}, \quad . \quad . \quad (183)$$

or unity at a sufficient distance. Moreover, neglecting relative order z^{-1},

$$\phi_{nr} = [\phi]_{m=z} - iz^{\frac{1}{3}} \beta \left(\frac{\partial \phi}{\partial m}\right)_{m=z},$$

so that the imaginary part of ϕ_{nr} may be written in the form

$$-\iota z^{\frac{1}{3}} \beta \left(\frac{\partial \phi_{nr}}{\partial m}\right)_{m=z} = -\iota z^{\frac{1}{3}} \beta \left(\sin^{-1}\frac{a}{r} - \frac{\pi}{2}\right) \quad . \quad (184)$$

on reduction.

But for ϕ_n we must write

$$\phi_n = \frac{\pi}{6} + \frac{1}{\mathrm{R}_n}(z-m) + \frac{\partial}{\partial z}\frac{1}{\mathrm{R}_n}\cdot\frac{(z-m)^2}{2} + \ldots \qquad (185)$$

where $\mathrm{R}_n{}^{-1}$ and its derivates are taken at $z=m$, the derivates being found from

$$\mathrm{R}_n = \frac{m^{\frac{1}{3}}}{3^{\frac{5}{6}}\pi^{\frac{1}{2}}}\left\{\Gamma\left(\frac{1}{6}\right) + \Gamma\left(\frac{1}{2}\right)(m-z)\left(\frac{24}{m}\right)^{\frac{1}{3}} + \ldots\right\} \qquad (186)$$

Thus

$$\mathrm{R}_n = \frac{m^{\frac{1}{3}}\Gamma(\frac{1}{6})}{3^{\frac{5}{6}}\pi^{\frac{1}{2}}}, \quad \frac{\partial}{\partial z}\frac{1}{\mathrm{R}_n} = -\left(\frac{1}{\mathrm{R}_n{}^2}\frac{\partial \mathrm{R}_n}{\partial z}\right)_{z=m} = \frac{6.3^{\frac{1}{6}}\pi^{\frac{1}{2}}\Gamma(\frac{1}{2})}{\Gamma^2(\frac{1}{6})m^{\frac{2}{3}}},$$

the latter having an order $m^{-\frac{2}{3}}$. The higher derivates of $\mathrm{R}_n{}^{-1}$ thus formed rise successively in order of smallness by $m^{-\frac{1}{3}}$. They are multiplied by successive powers of $z-m$ or $\iota z^{\frac{1}{3}}\beta$ in (185), so that, effectively,

$$\phi_n - \frac{\pi}{6} = \frac{(z-m)\pi^{\frac{1}{2}}3^{\frac{5}{6}}}{\Gamma(\frac{1}{6})m^{\frac{1}{3}}}\left\{1 + \iota\alpha_1\beta + \alpha_2\beta^2 + \ldots\right\}, \qquad (187)$$

where the α's are real and numerical. The series in brackets is of course not convergent, being asymptotic in the usual sense. By restricting the series to one or two terms, we obtain the order of magnitude of the imaginary part of ϕ_n, which is $+\iota\beta\delta$, where δ is positive, real, and numerical, and also not large. Thus the imaginary part of ϕ_n is of no order in $z^{\frac{1}{3}}$, and may be ignored in comparison with that of ϕ_{nr}.

If ϕ_n were needed explicitly, the expansions of the Bessel functions in terms of Airy's integral and its associates would be used, as in the investigation of the transitional region. But this determination of ϕ_n may be omitted, as it leads to no points of special interest.

Finally, therefore, $\phi_n - \phi_{nr}$ has an imaginary part which is given effectively by $+\iota z^{\frac{1}{3}}\beta\cos^{-1}a/r$ from (184), and a real part which contributes only to the phase of the disturbance in the shadow. A discussion of this phase, whose expression is cumbrous, does not serve any useful purpose, and may be omitted also.

It follows that the real part of $-\iota(\phi_n - \phi_{nr})$ is $z^{\frac{1}{3}}\beta\cos^{-1}a/r$, and this introduces a factor exp. $z^{\frac{1}{3}}\beta\cos^{-1}a/r$ into the amplitude of the disturbance at a distance r. This factor is unity, as it should be, when $r=a$. The amplitude of γ at a point of orientation θ on the surface was, by (99),

$$A = k^2(ka)^{-\frac{5}{6}}(2\pi \sin\theta)^{\frac{1}{2}}\beta^{-1}e^{-(ka)^{\frac{1}{3}}\beta\theta}, \quad . \quad . \quad (188)$$

where ka is z as usual.

The amplitude at distance r and orientation θ is accordingly

$$\frac{aA}{r}\left(\frac{R_{nr}}{R_n}\right)^{\frac{1}{2}} \exp. (ka)^{\frac{1}{3}}\beta \cos^{-1}\frac{a}{r}, \quad . \quad . \quad . \quad (189)$$

where by (183) and (186)

$$R_{nr} = (1 - a^2/r^2)^{-\frac{1}{2}}$$

$$R_n = z^{\frac{1}{3}}\Gamma(\tfrac{1}{6})/3^{\frac{5}{6}}\pi^{\frac{1}{2}}.$$

Finally, therefore, the amplitude in the shadow becomes

$$\frac{\sigma k}{r}(\sin\theta)^{\frac{1}{2}}\left(1 - \frac{a^2}{r^2}\right)^{-\frac{1}{4}} e^{-(ka)^{\frac{1}{3}}\beta\left(\theta - \cos^{-1}\frac{a}{r}\right)}, \qquad (190)$$

where $\beta = \cdot 696$, and $\sigma = 2^{\frac{1}{2}}3^{\frac{5}{12}}\pi^{\frac{3}{4}}/\beta\sqrt{\Gamma(\frac{1}{6})}$.

Thus the magnetic force at a great distance is inversely proportional to r, as it should be.

The numerical value of σ is 3·21.

The mode of derivation of this formula is still valid for points near the axis of the shadow, where $\theta = \pi$, and we conclude that the effect on the axis is absolutely zero, as it would be if the sphere were absent. This result has an analogy with the usual geometrical theory of Poisson's disk, on which plane waves impinge. In the axis of the shadow thrown by the disk, there is an effect of the same order as though the disk were absent. The theoretical description of this phenomenon was one of the earliest successes of the wave theory of light. A description of the phenomenon on the strict basis of the electromagnetic theory has not been given.

When plane waves fall on a large conducting sphere, the results of an unpublished investigation by the writer indicate brightness on the axis of the shadow, which should be capable of experimental detection at a sufficient distance. This experiment has been performed by Lord Rayleigh *, who found a bright spot on the axis, at a sufficient distance, which could be clearly seen with a magnifying lens.

Accordingly, there is an essential difference between the cases of incident plane waves, and of a Hertzian oscillator placed close to the sphere, in so far as the axis of the shadow is concerned, but in each case the effect has the same character as though the sphere were absent.

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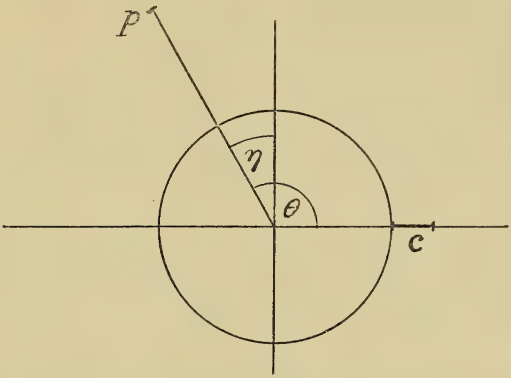
* *Vide* Proc. Roy. Soc. 1904, p. 40.

An examination of the exponential factor of (190) is instructive. In the shadow, $\theta - \cos^{-1} a/r$ must be positive,



attaining its minimum when $r \cos\theta = a$, that is to say, on the line already shown to be the centre of the transitional region, in which diffraction-bands have been indicated.

At a remote distance the amplitude is proportional to

$$\sqrt{\cos\eta}\, e^{-(ka)^{\frac{1}{3}}\beta\eta},$$

where η is the angle in the figure.

The evanescence of the exponent in the transitional region indicates the change in character of the solution, which must, for that region, be found by the method previously used for the purpose since the method of residues fails.

We see that for large orientations, the use of raised receivers of the waves does not assist diffraction, to a measurable extent, in giving an effect capable of detection, and our earlier conclusion, that the explanation of long-distance telegraphy must be sought elsewhere, is rendered more emphatic.

LXXVIII. *The Distribution and Quality of the Secondary Röntgen Radiation from Carbon.* By H. PEALING, *M.Sc.*, *the University of Liverpool* [*].

I. *Preliminary.*

IF a beam of Röntgen rays of ordinary penetrating power fall on a substance of low atomic weight such as carbon, then this becomes a source of Röntgen rays, which are emitted in all directions and are of the same penetrability as the primary beam. Such a radiation is said to be scattered.

[*] Communicated by Prof. L. R. Wilberforce.

The intensity of the secondary rays from the carbon varies in different directions. In directions nearly parallel to the incident primary beam the intensity is greatest, while in a direction at right angles it is least.

The objects of this investigation were:—

(1) To find the variation in the distribution of the rays emitted in the horizontal plane containing the primary rays, when (*a*) the primary beam was gradually hardened, and when (*b*) the harder portions of the primary beam were used; and

(2) To compare the absorbability of the carbon radiation with the primary producing it, and to find how the difference alters when the primary is made very hard and only the hard portions of it are used.

II. *Theory of the Distribution of the Secondary Radiation from Carbon.*

Several investigators, notably Barkla*, have worked out some results of the elementary theory of the distribution of a scattered radiation, on the assumption that the rays consist entirely of electromagnetic impulses travelling with the velocity of light.

A single æther pulse travelling in a horizontal direction with the direction of its electric force vertical, will cause an atom of carbon to radiate the rays with equal intensity in all directions in the horizontal plane containing the atom; while the radiation set up in it by a pulse having the direction of electric force horizontal will be zero in a direction at right angles to the beam, and a maximum in the same direction as the primary rays. When the incident beam is on the whole unpolarized, the intensity of the scattered radiation in this horizontal plane in a direction making an angle α with the primary beam will be

$$I_\alpha = I_{90}(1+\cos^2\alpha),$$

where I_α and I_{90} are the intensities in directions making angles of α and 90° respectively with the primary beam.

This law was tested by Barkla and Ayres†, and found by them to be accurately obeyed for all values of α greater than 30° when the primary beam is very soft. With angles less than 30° the ratio was considerably greater than the value predicted by theory. When the primary beam is harder, they found that the results do not agree with this simple theory.

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* Barkla, Phil. Mag. Feb. 1901, pp. 288–296. Barkla and Ayres, Phil. Mag. Feb. 1911, pp. 270–278.

† *Loc. cit.*

Now it is well known that if a primary beam of Röntgen rays of ordinary penetrating power falls on an element of higher atomic weight than 40, then that substance emits, in addition to the relatively feeble scattered radiation, a secondary radiation whose penetrating power is characteristic of the particular element and does not depend in any way on the character or intensity of the incident primary rays. Barkla has called this a fluorescent radiation. Although a fluorescent radiation has not yet been identified in the case of carbon, yet there is good reason for predicting that if a very penetrating beam of Röntgen rays fell on it a fluorescent radiation would be given off. The fluorescent radiation has entirely different properties for the scattered radiation. Two laws will be referred to frequently, the first governing the production and the second governing the distribution of fluorescent radiation. The first was proved by Barkla and Sadler and the second by Barkla.

(1) The fluorescent radiation of a particular element is only excited by a radiation which is harder than itself.

(2) The value of the ratio $\frac{I_\alpha}{I_{90}}$ of it is unity for all directions.

The laws of distribution for the fluorescent and scattered radiations are thus entirely different, and so it is necessary to consider in what way the superposition of a hard fluorescent radiation will affect the value of $\frac{I_\alpha}{I_{90}}$ for whole beam.

If the primary beam is very soft, none of the harder fluorescent carbon radiation will be excited and the ratio should be $(1+\cos^2\alpha)$. When the beam is harder, the fluorescent radiation will then be excited, and any given atom of carbon will emit it uniformly in all directions.

The total radiation, it is easy to see, will give a ratio less than $(1+\cos^2\alpha)$. As the beam is made very penetrating indeed, the proportion of fluorescent to scattered radiation is very largely increased so that for a very penetrating beam the ratio should approximate to unity. As well as the very penetrating fluorescent radiation, it is highly probable that the carbon emits an exceedingly soft fluorescent radiation. The intensity of this per unit area of a thick radiation must be extremely small compared with the intensity per unit area of the scattered radiation, because it will be very readily absorbed in the radiator itself, and all that emerges into the air will have been generated in an extremely thin surface layer and will be readily absorbed by the air. The scattered radiation, on the other hand, will penetrate an enormously greater thickness of carbon. It is easy to see that so long as thick radiators are used, the effect of the soft fluorescent radiation from carbon will have little or no influence on the value of $\frac{I_a}{I_{90}}$.

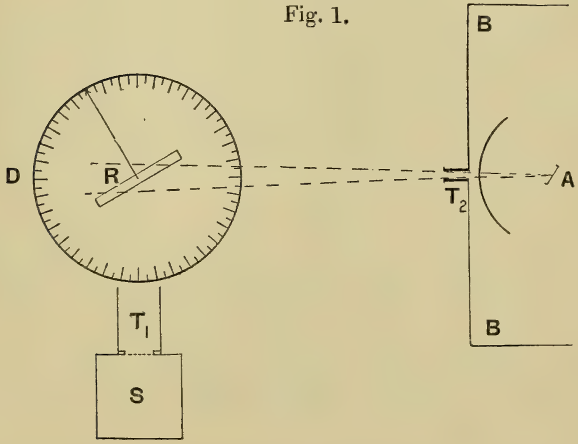
Carbon also emits, under the influence of a beam of Röntgen rays, very easily absorbed corpuscular rays. It has been shown by a number of investigators that these are absorbed in a few millimetres of air. For this reason no corpuscular rays will reach the measuring electroscope, and so the value of $\frac{I_a}{I_{90}}$ observed by experiment does not depend in any way on the direct action of this easily absorbed radiation. We shall see later that there is a strong probability that this corpuscular radiation, although very little of it emerges from the radiator, yet produces in the radiator itself another radiation in appreciable quantities. This we shall call an "extra" radiation.

III. *Theory of the Absorbability of the Secondary Radiation from Carbon.*

In many of the experiments very penetrating beams were used, so that we may reasonably expect that the very penetrating fluorescent radiation will be present in the secondary beam excited by them. The presence of the hard radiation should very considerably modify the absorbability of the secondary radiation emitted. The scattered radiation from the carbon is of the same penetrating power as the primary which excites it. Thus the secondary beam emitted by a very thin sheet of carbon will be of the same penetrating power as the primary, when that primary is very soft, because the secondary radiation is wholly scattered and any soft fluorescent radiation which is excited will not reach the measuring electroscope. As the primary beam becomes harder, the very hard portions may be slightly harder than the hard fluorescent carbon radiation. In this case these hard portions will excite the fluorescent radiation. The secondary beam emitted will then consist of the scattered radiation which, although it is softer than the hardest portion of the primary, will yet be very considerably harder than the primary beam taken as a whole. These two components, the one just as penetrating, and the other much harder than the primary, will together give a secondary beam harder than the primary exciting it. As the primary beam is made harder the secondary beam should be much harder. The percentage difference in hardness will depend on the transformation coefficient which is the ratio of the energy in the secondary beam excited by a primary beam traversing unit thickness of material to the energy in the primary beam, supposing the primary beam to be maintained in some way of constant intensity during its passage through the substance. In the case of copper the transformation coefficient is so large that the ionization produced by the fluorescent radiation is 300 times that produced by the scattered beam when beams of ordinary penetrating power are used. Now although it is very unlikely that the transformation coefficient for the hard fluorescent carbon radiation is as high as for copper radiation, it is clear that if we have a primary beam sufficiently hard, the proportion of fluorescent radiation to scattered will be quite considerable and so the secondary beam would be much harder than the primary. When the primary beam becomes so hard that taken as a whole it is harder than the fluorescent carbon radiation, then the secondary carbon radiation will be softer than the primary, as is the case with copper radiation when we use an ordinary Röntgen-ray bulb. To sum up, we should expect that the secondary beam should be just as penetrating as the primary, then much harder than it, gradually approaching an almost constant value, while the primary getting harder all the time soon overtakes it, becoming just as hard and finally much harder.

IV. *Description of Apparatus used to measure the Value of* $\frac{I_a}{I_{90}}$.

Fig. 1.



The plan of the apparatus is shown in fig. 1. The carbon radiator R was ·94 cm. thick and 8·9 cm. square. It was held in the vertical plane by means of a thin brass rod which was capable of rotation in a circular block of wood D. The rod was provided with an index (shown in diagram) moving on a scale marked in divisions of 5 degrees, to determine the angle the plane of the radiator made with the primary beam. The secondary electroscope S, which was of the simple Wilson type, was attached to a block of wood, and was capable of rotation about the same axis as R. The electroscope which was used to standardize the primary beam was placed on the top of the lead box used to contain the bulb, and a vertical beam of the rays was admitted through a window of thin tissue-paper at the base of the electroscope. The width of this beam could be varied by a screw.

The secondary electroscope was fixed so that the perpendicular to the centre of the window (consisting of aluminium foil between two sheets of tissue-paper) admitting the rays passed through the axis of rotation of the radiator, thus ensuring that S was always symmetrical about the axis of rotation of the radiator, no matter what angle the axis of the electroscope made with the direction of the primary rays. It was provided with an index moving over the scale on D to measure this angle. The window of S was 2·4 cm. wide and 5·5 cm. high, and was distant from the centre of R 17 cm. S was provided with a lead tube T lined with aluminium, which admitted nearly all the rays from the carbon which would have fallen on the window of S but cut off most of the air and other stray radiations. These were also limited by the tube T_2 which allowed a beam of rectangular cross-section to fall on the radiator. The anticathode A of the bulb contained in the lead box B was distant from the centre of R 40 cm. The bulb was held in a wooden stand with the cathode stream inclined at an angle of 45° to the vertical.

This was a very convenient arrangement, and was devised by Sadler and used by him with Bowen three years ago to determine the variation of $\frac{I_\alpha}{I_{90}}$, using soft beams. Later the writer was asked by Sadler to complete the experiments; but on the publication of an investigation on the same subject and by essentially the same method by Barkla and Ayres, on his advice the experiments were abandoned. Later, the writer observed several apparent anomalies in the results, so the apparatus was reconstructed. The dimensions are given above. They are slightly different from these of the former apparatus.

V. *Method of Experimenting.*

The radiator was set at an angle of 30° with the beam. S was then placed with its axis making 150° with the primary beam, and the ratio of the secondary to the primary deflexion obtained. S was then set with its axis at right angles to the primary and on the same side of the radiator, and a similar ratio found. Dividing the first ratio by the second, we get the value of $\frac{I_{150}}{I_{90}}$. Several corrections are necessary, and of these two will vary as the hardness of the primary beam varies, namely, the correction due to

(1) The polarization of the primary beam.

(2) The secondary radiation from the air and tertiary radiation from surrounding objects.

When a bulb is very soft we have a maximum amount of polarization, but with the cathode stream inclined at 45° to the vertical it is very unlikely that the theoretical value of $\frac{I_{150}}{I_{90}}$ will be greater than 1·795—an increase of only $2\frac{1}{2}$ per cent. of its value with an unpolarized beam. When the beam is very hard it exhibits no polarization.

The correction due to the air and other stray radiations and the normal leak of the electroscope were rendered negligible by the use of a thick radiator which gave rapid deflexions. Since the radiator is set so that the normal to it bisects the two directions along which we successively measure the intensity of the secondary radiation, then the radiation from any small portion of carbon in the thick radiator will traverse exactly the same thickness of carbon; and so the radiation of any particular absorbability will be absorbed by exactly the same amount by the material of the radiator, and the deflexions obtained will give the same ratio as if none of the secondary radiation was absorbed in the carbon or air. The total air and other stray radiations were never more than 4 per cent. of the total deflexion obtained; and as a large portion of this was cut down by the carbon radiator itself, and their ratio in the two directions approximately the same as for the carbon radiator, they were therefore neglected.

This was also justified by the following experiment. A very thin sheet of pure copper was mounted on an aluminium frame and then set with its plane making an angle of 25° to the primary beam. The copper was arranged so that the rays fell on the central portion of it. None whatever fell on the frame. The ratio $\frac{I_{40}}{I_{90}}$ was found to be 1 : 1·00; and when the experiment was repeated the ratio was found to be 1: 1·004, no correction being made. This agreed very well with the value found by Barkla and Ayres * after making the necessary corrections.

There are two corrections which do not vary with the hardness of the rays.

(*a*) The observed value of I_{90} will always be greater than that given by theory because the radiator subtends a considerable angle to the window of the electroscope, so that when the axis of the electroscope is 90° to the direction of the beam the rays entering the window from the edges of the carbon make angles considerably less or more than 90° with the beam. The average of $(1+\cos^2\alpha)$ for all the rays was calculated and found to be 1·015. The errors due to this cause in the direction $\alpha=150°$ or $\alpha=40°$ are negligible.

(*b*) The window of the electroscope subtends a considerable angle in the vertical direction with the radiator. This will make the value of I_{150} observed less than theory predicts. It was calculated that the average value of $(1+\cos^2\alpha)$ for all the rays when the axis of the electroscope made an angle of 150° with the rays was 1·735.

We should expect that owing to all these corrections the value of $\frac{I_{150}}{I_{90}}$ observed for the scattered rays should be 1·75 when the beam is soft and 1·71 when the beam is hard.

As it would have been very laborious to have obtained the variation of $\frac{I_\alpha}{I_{90}}$ for a large number of directions, the investigation was confined almost wholly to two values of α, namely 150° and 40°. The results for $\frac{I_{150}}{I_{90}}$ and $\frac{I_{40}}{I_{90}}$ should give results typical of all values of α greater than 90° and less than 90° respectively.

These angles give ratios whose values by theory should be 1·75 and 1·58 respectively.

VI. *Results.*

(a) *For values of* $\frac{I_{150}}{I_{90}}$.

Experiments were tried with the bulb very soft. It was found invariably that the ratio observed was lower than 1·75; the results varying from about 1·55 to 1·65, according to the degree of softness attained, the lower ratio being obtained with a very soft bulb. With harder rays, when the secondary beam was cut down in each case to about two-thirds of its original value, the ratio was considerably increased, the average of a number of values being 1·69. The increase in the ratio for the harder portion of the secondary beam was confirmed by a large number of experiments. The result may be explained by the fact that when a bulb is most completely polarized, the harder portion of it is more completely polarized than the softer portions. This, however, would have to be very pronounced to produce so large an effect on the ratio. A second and more probable explanation is that the specimen of carbon used which was supplied as pure contains a very slight proportion of iron. Let us suppose that the proportion of iron radiation in the direction $\alpha=90°$ is 10 per cent. of scattered radiation, then the ratio observed would be $\frac{1\cdot85}{1\cdot10}=1\cdot68$ instead of the value 1·75. The sheet of aluminium of thickness 0·015 cm. used to cut down the secondary rays would cut more than 90 per cent. of the iron radiation, and so the ratio would jump up to 1·75. Now only a very small portion of iron will be necessary to produce this percentage of the ionization—something of the order 0·1 per cent. A numerical example, giving an extreme case, will make this clearer. Suppose we have incident on a very thin carbon radiator the secondary radiation from nickel; let the amount of iron be w grs. per unit mass of the carbon. The proportion of energy in the scattered beam to the iron fluorescent beam is $\cdot2 : \frac{526}{7\cdot76}w=\frac{\cdot2}{67\cdot8}w$.

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* *Loc. cit.*

$\cdot2=$the coefficient of scattering.

526 is the transformation coefficient of nickel radiation incident on iron and 7·76 is the density of iron. The ratio of the ionization these two radiations would produce in a thin layer of air is $\frac{\cdot2}{67\cdot8}w\times\frac{239}{159\cdot5}$ equals approximately $100w$. ·239 and 159·5 are the absorption coefficients of iron and nickel radiation respectively in aluminium.

Hence if the ionization due to the iron is about 10 per cent. of that due to the carbon, then there must be present in the carbon

0·0002 gr. of iron per gram of carbon.

Now the specimen of carbon used contained a small amount of iron, so this explanation of the rise of the value of I_{150}/I_{90} with hardness of the secondary is the more likely one.

When the bulb is very soft indeed the proportion of iron radiation present will be considerably increased, as for hard beams the scattered radiation will not be absorbed by the carbon to nearly the same extent as the iron radiation. Thus we explain the fact that the ratio is low for very soft beams. Table I. is typical of the results obtained when rays of moderate penetrating power were used.

TABLE I.

Absorption of the secondary beam in direction 150° to primary beam by aluminium 0·15 mm. thick.	Value of $\frac{I_{150}}{I_{90}}$ for whole beam.	Value of $\frac{I_{150}}{I_{90}}$ for beam subsequent to absorption in column 1.
30·7 per cent.	1·62	1·67
29·0 ,,	1·60	1·70
26·3 ,,	1·54	1·60

This also shows clearly that the ratio drops as the rays become harder, thus confirming the result predicted by theory that as the beam became harder the ratio would get less owing to the presence of hard fluorescent carbon radiation. When the primary beam was cut down by aluminium before falling on the radiator, somewhat different results were obtained. These are shown in Table II.

TABLE II.

Thickness of aluminium absorbing primary rays.	Values of $\frac{I_{150}}{I_{90}}$.	Thickness of aluminium absorbing secondary rays.
none.	1·63	none.
0·95 mm.	1·64	none.
3·2 mm.	1·68	none.
none.	1·41	3·2 mm.

The figures in column 2, Table II. give the values of $\frac{I_{150}}{I_{90}}$ observed when the primary has been deprived of its softer constituents by the thickness of aluminium given in column 1.

It is seen that $\frac{I_{150}}{I_{90}}$ increases with the hardness of the rays falling on the radiator. That this increase in the ratio is not due to the harder portions of the secondary radiation having a high ratio was shown by the low value obtained (1·41) when the secondary rays were cut down instead. If we use an extremely penetrating beam, then the ratio falls when only the hard portions of it fall on the radiation.

The decrease in the value of $\frac{I_{150}}{I_{90}}$ for the hard portions of the secondary beam is shown clearly in Table III.

TABLE III.

Thickness of aluminium absorbing primary rays.	Values of $\frac{I_{150}}{I_{90}}$.	Thickness of aluminium absorbing secondary rays.	Approximate per cent. of the secondary beam absorbed by aluminium in column 3.
none	1·64	none	none
none	1·66	0·15 mm.	29 per cent.
none	1·53	0·95 mm.	70 per cent.
none	1·53	1·6 mm.	81·4 per cent.
none	1·40	3·2 mm.	92·3 per cent.
3·2 mm.	1·67	none	none

The values of $\frac{I_{150}}{I_{90}}$ shown in column 2 indicate a steady fall in value as the hard portion of the secondary beam is used, if we neglect the initial rise due to the absorption of the iron radiation. The steady rise in the ratio when the hard portions of a primary beam are used, indicate that the fluorescent carbon radiation is only excited by the very hard portions of them. The increase in the ratio is explained by the existence of the "extra" radiation of which more will be said presently.

(b) *Results for Values of* $\frac{I_{40}}{I_{90}}$.

These results were all invariably greater than 1·58 for all degrees of hardness of the bulb, the discrepancy increasing with the hardness of the rays used. Table IV. shows the variation of the ratio with the hardness of the secondary radiation used.

TABLE IV.

Thickness of aluminium absorbing secondary rays.	Values of $\frac{I_{40}}{I_{90}}$.	Absorption of secondary rays by thickness of aluminium given in column 1.
none	1·69	none
0·15 mm.	1·72	14·9 per cent.
0·95 mm.	1·74	55 per cent.
1·6 mm.	1·88	67 per cent.
3·2 mm.	1·97	84 per cent.

When the hard portions of a very hard beam were used the ratio fell to 1·75.

Somewhat similar results were obtained when the hard portions of a hard primary beam fell on the radiator.

They are shown in Table V.

TABLE V.

	Thickness of aluminium absorbing the primary beam.	Values of $\frac{I_{40}}{I_{90}}$.	Thickness of aluminium absorbing the secondary beam.
(*a*)	none	1·67	none
	0·15 mm.	1·69	none
	0·95 mm.	1·72	none
	1·6 mm.	1·88	none
	3·2 mm.	1·80	none
	none	2·03	3·2 mm.
(*b*)	none	1·67	0·15 mm.
	3·2 mm.	1·54	0·15 mm.

Table V. (*a*) gives the results for a moderately hard bulb, while (*b*) gives the results for a very hard bulb. In the latter experiments the secondary beam was absorbed by thin aluminium to get rid of the iron radiation present.

It is seen that the ratio rises with the hardness of the beam, but when very hard rays are used the ratio drops again.

All these results can be explained by the existence of an "extra" carbon radiation. Crowther* has argued that it is an indirect effect of the corpuscular carbon radiation. It is easy to see that it will not differ very much from the primary in penetrating power. Those corpuscles which are stopped instantaneously will give rise to Röntgen rays of the same penetrating power as the primary [*]. Since some of the corpuscles will be stopped much more quickly than others and those which are stopped late in their career will have lost some of their initial velocity, the Röntgen rays produced by a corpuscle will in general be softer than the primary pulse expelling the corpuscle.

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* Crowther, Proc. Phil. Soc. Camb. pp. 534–539 (1912).

If we assume that this "extra" radiation is very much greater in amount in the forward direction than in the direction opposite to the direction of the primary rays, and that the ratio of the amount of extra to the amount of scattered radiation increases with the hardness of the rays used, we can explain all our results. These suppositions seem justified by the results of Gray's experiments on the γ radiation excited by the β rays from radium [†].

First consider the results given in Table II. The hard portions of the primary will excite in the carbon

(*a*) pure scattered radiation of the same penetrating power as the primary, the value of $\frac{I_{150}}{I_{90}}$ for which does not vary with increase in hardness of the rays.

(*b*) The "extra" radiation softer than the primary, the value of $\frac{I_{150}}{I_{90}}$ for which increases as the hardness of the rays used increases, and

(*c*) hard fluorescent radiation. which is only produced by the very hard portions of the beam and in relatively small amounts.

As the fluorescent is only present in small amounts we explain the increase in ratio when only the hard rays fall on the radiator.

When the secondary rays are absorbed the fluorescent radiation will be present in much larger proportions, as both the "extra" and scattered radiation, and particularly the "extra" [‡], are softer than the fluorescent radiation, and are, therefore, absorbed in much larger proportions. This explains the results in Table III.

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[*] Whiddington, Proc. Phil. Soc. Camb. p. 329 (1911).

[†] J. A. Gray, Proc. Roy. Soc. A. vol. lxxxvi. pp. 513–529.

[‡] The fact that the extra radiation is softer than the primary producing it is not necessary to the argument.

The extra radiation is certainly softer when a homogeneous beam is used, but it is very unlikely that this is true for a heterogeneous beam, as the ratio of the energy in the "extra" radiation to that in the primary increases with an increase in the hardness of the primary. All that is necessary is that the extra radiation is softer than the fluorescent, which is the case as the fluorescent is harder than any of the primary beams used, and also that the "extra" radiation is very small in amount compared with the scattered radiation, which is the case for the radiation in this direction.

In the case of the forward radiation, the amount of the "extra" radiation is much greater than the sum of the other two, and so the fluorescent radiation has very small influence on the ratio unless very penetrating rays are used. This explains at once the results in Table V. when the hard portions of a primary beam are used.

The increase in the ratio of the extra radiation masks the decrease in the ratio of the remainder due to the presence of hard fluorescent carbon radiation until very penetrating rays are used.

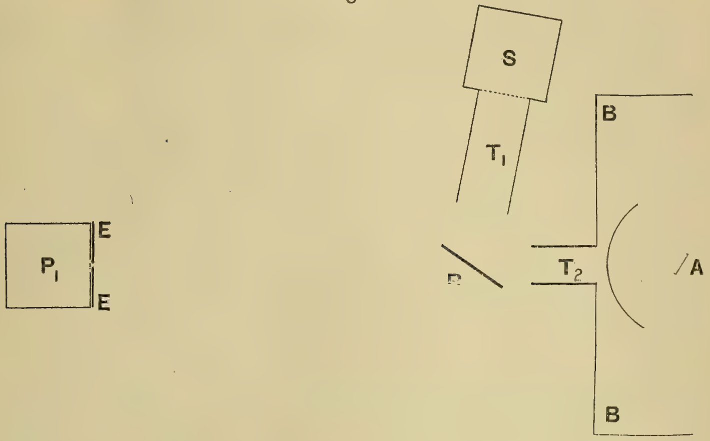
The results given in Table IV. may be explained best by considering the effect of the portions of the beam harder than the carbon fluorescent radiation separately. This hard portion will excite hard fluorescent, and also a considerable quantity of "extra" radiation. We should, therefore, expect a low value of $\frac{I_{40}}{I_{90}}$ for this portion of the secondary beam after absorption by the thick aluminium. The other portion of the primary beam, and especially the hard part of it, will produce a very large amount of extra radiation. The ratio $\frac{I_{40}}{I_{90}}$ for the soft part of this portion of the beam will then be much less than for the hard part of it. Hence, when this portion of the beam is sent through thick aluminium the ratio $\frac{I_{40}}{I_{90}}$ for the portion that emerges will be much greater than for the total beam before passing through the aluminium. Now as the amount of this passing through the aluminium will be large compared with the part due to the very hard rays of the beam, it is clear that the ratio for the two together will alter in the same direction as the ratio for the softer portion. That is, the ratio will rise. When the proportion of the hard rays increases the ratio will fall again. Hence both the results indicated in Table IV. are explained.

There remains now to be explained a result which has not yet been mentioned above, namely, when a thin radiator is used the ratio in the forward direction is higher. The radiator used was thin, ·3 mm., but gave a deflexion of about the same magnitude as the thick radiator. The explanation is that this is due to the smaller percentage of fluorescent radiation present in the former case. The proportion in the case of the thick radiator would be between 2 and 3 times that for the thin radiator.

VII. *Description of Apparatus used to Measure the Absorbabilities of the Secondary and Primary Beams.*

The plan of the apparatus is shown in fig. 2.

Fig. 2.



The electroscope P_1 was provided with a lead screen E which had a small circular hole 4 mm. in diameter, allowing a small pencil of primary rays to enter it. The electroscope S provided with a lead tube T, lined with aluminium 0·15 mm. thick, measured the amount of secondary radiation given off by the radiator R. Another electroscope P_2, not shown in diagram, was placed on the top of the lead box B containing the bulb A, and measured the intensity of the primary rays. The tube T_2, admitting the rays on to R, was made of lead and was lined with aluminium 0·3 cm. thick. Its dimensions were 6·5 cm. long, 3·3 cm. wide, and 5·5 cm. deep. The tube T_1 was 11·5 cm. long, 5 cm. wide, and 4·5 cm. high, and was distant from the centre of the radiator R 16·5 cm. The window of P_2 was 57 cm. from the anticathode of the bulb.

VIII. *Method of Experimenting.*

(a) *Measurement of the absorbability of the primary beam.* A lead screen with a small circular hole was placed at the side of T_2 nearest the bulb, and was of such a size and position that the central portion only of the primary beam it admitted passed through the orifice of E. The percentage absorption of the primary beam by successive sheets of thin aluminium was then obtained, using the electroscopes P_1 and P_2. The lead screen, 3 mm. thick at T_2, was placed there in order to screen E from the secondary radiation from the glass of the bulb. It was necessary to have the orifice of E small, otherwise the saturation current would not be obtained, a source of error that was kindly pointed out to me by A. I. Steven, M.A. It is clear, however, that the orifice of E could not be much reduced in size, because the marginal portions of the beam entering S, which have had their softer components absorbed by the lead screen E, will bear an appreciable ratio to the total beam.

(b) *Absorbability of the Secondary Beam.*—The radiator R was placed in position and the screen at the tube T_2 taken away. The same sheets of aluminium were used to determine the percentage absorption of the secondary radiation from R. The air and other stray radiations were allowed for. Now it is at once obvious that this will not give an absolute comparison of the absorbabilities of the primary and secondary beams. We shall have to correct for the absorption of the two beams in the air and radiator, and also for the obliquity of the secondary beam. If, however, we compare these absorbabilities, using a thin radiator and the bulb only when very soft, we obtain a measure of the correction necessary, as it has been shown by much direct and by an overwhelming amount of indirect evidence that the scattered radiation is of the same penetrating power as the primary[*]. Much thicker radiators could be used when experimenting with the hard portion of the primary beam, as then the beam is not very heterogeneous.

IX. *Results for the Absorbabilities of the Primary and Secondary Radiations.*

When the bulb was very soft the results in Table VI. were obtained after subtracting the air effect, using four sheets of

TABLE VI.

	Percentage absorption of beam by aluminium 0·15 mm. thick.	Percentage absorption of beam by aluminium 0·15 mm. thick subsequent to absorption in column 1.	Nature of beam.
(*a*)	32·15	25·55	Secondary.
	31·8	24·6	Primary.
	33·15	24·35	Secondary.
(*b*)	29·95	23·75	Primary.
	27·8	21·9	Secondary.

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[*] Barkla, Phil. Mag. Sept. 1911, pp. 396–412.

filter-paper as radiator. Filter-paper was used as thin sheets of carbon are not readily obtained. The fact that filter-paper contains oxygen and hydrogen as well as carbon does not affect the argument.

The air effect for the secondary beam was about 26 per cent. of the total. Table VI. (*a*) indicates that the secondary beam is 2 per cent. softer than the primary beam. We may, therefore, assume that the obliquity, &c. correction for the secondary beam amounts to 2 per cent. When the primary beam was harder the results given in Table VI. (*b*) were obtained. The secondary beam was then appreciably harder than the primary, indicating that a hard fluorescent radiation was given off by the filter-paper. The probability is strong that this is due to the carbon contained in it. When a thick piece of carbon was used as radiator and the hard portions of a hard beam allowed to fall on it, the results could not be so simply deduced as it absorbed about 50 per cent. of the beam incident on it. As, however, the beams used were not very heterogeneous, the correction due to the absorption of the secondary and primary beam was not great. It was found that when a moderately hard beam was used, the hard portions of it produced a radiation in the carbon which after absorption in the radiator itself was approximately of the same penetrating power as the primary. The thickness of aluminium successively used as test pieces were 0·15, 0·8, and 1·4 mm. The corrections due to the absorption of the primary and secondary beam by the radiator would make the secondary radiation softer than the primary. As, however, there will be a considerable amount of extra radiation emitted which is softer than the primary it is impossible to say at present whether this softening is due to the extra radiation or to the fluorescent radiation, or to both jointly. Further experiments need to be made.

The experiments on the absorption of the carbon radiation have so far been confined to one particular direction, viz., about 90° to the direction of the beam. A number of experiments were made using the apparatus shown diagrammatically in fig. 1. It was found that the radiation in the direction $\alpha=90°$ was softer to a first sheet than the radiation in the direction $\alpha=150°$. The results of a number of values were averaged, and are given in Table VII. (p. 782).

These results, though apparently anomalous, simply mean that the softer portions of the beam have a low value of $\frac{I_{150}}{I_{90}}$, as also have the very hard portions, which we have explained as being due to the presence of iron and carbon

TABLE VII.

	Angle the direction of the portion of the secondary beam considered makes with primary beam.	Percentage absorption by aluminium 0·15 thick subsequent to absorption in column 3.	Amount previously absorbed.
(*a*)	90	32·8	none
	150	30·5	none
(*b*)	90	25·5	none
	150	23·6	none
	90	13·6	25·5
	150	15·6	23·6

(*a*) gives the results for a thin carbon radiator, 3 mm., and (*b*) for a thick one.

fluorescent radiations respectively. The softer iron radiation would make the radiation at right angles to the primary beam softer, while the fluorescent carbon radiation would make it harder than the radiation in a direction making 150° with the primary beam.

An aluminium radiator was also tried. The values of $\frac{I_{40}}{I_{90}}$ and $\frac{I_{150}}{I_{90}}$ for it were greater than for carbon. This indicated a greater amount of extra radiation from aluminium, but the evidence is not conclusive, as the hard fluorescent radiation of aluminium will be much harder than that of carbon, and will be excited in much smaller proportions. The absence of the fluorescent radiation in the aluminium would make the ratio $\frac{I_{40}}{I_{90}}$ and $\frac{I_{150}}{I_{90}}$ greater than for carbon.

Summary.

1. The variation of the distribution of the scattered radiation produced in carbon by beams of Röntgen rays differing in penetrating power has been investigated, and unexpected results have been obtained.

(*a*) When the hard portions of a hard primary beam were used the ratios $\frac{I_{150}}{I_{90}}$ and $\frac{I_{40}}{I_{90}}$ both increased, but with very hard beams both decreased.

(*b*) The ratio $\frac{I_{150}}{I_{90}}$ was low and $\frac{I_{40}}{I_{90}}$ was high for the hard portions of the secondary beam.

(*c*) The amount of the forward radiation was always considerably greater than the radiation sent in a direction opposite to that of the beam.

(2) The results, though apparently contradictory, are very simply explained; as

(*a*) When the primary beam is soft the secondary beam consists of scattered radiation and an "extra" radiation which is softer than the primary. The proportion of extra radiation on the forward direction is very much greater than in the other direction.

(*b*) When the primary beam is hard the secondary beam consists of scattered radiation, a larger proportion of "extra" radiation than when the beam was soft, and hard fluorescent carbon radiation.

(3) Confirmation of these views has been obtained by a study of the relative absorbabilities of the primary and secondary beams.

George Holt Physics Laboratory,
July 31, 1912.

LXXIX. *Delta Rays produced by Beta Rays.*

By Norman Campbell, *Sc.D.*[*]

1. In several previous papers experiments[†] have been described which appear to prove conclusively that the quality of the δ rays emitted from solids under the action of α rays is independent of the velocity of the α rays and the nature of the solid. Accordingly this quality must be determined either by some structure which is common to all α rays (that is, by the nature of the helium atom of which all α rays consist) or by some structure common to all atoms which is concerned in the process of ionization of those atoms. The alternatives may be distinguished by discovering whether the action of ionizing agents other than α rays results in the production of similar δ rays.

2. When the literature of the subject was examined it appeared immediately that it was exceedingly probable that δ rays of a quality very similar to those produced by α rays were produced by the action of β or cathode rays. It was

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[*] Communicated by the Author.

[†] Phil. Mag. Aug. 1911, p. 276; Jan. 1912, p. 46; Oct. 1912, p. 527.

proved by Lenard[*] that under the action of β rays, with a velocity greater than 11 volts, all metals emitted a "secondary cathode radiation," the velocity of which was nearly the same for all substances and of the order of 10 volts. His results have been confirmed by many subsequent investigators, and especially by Gehrts[†], who finds that the quality of this secondary radiation is the same from whatever metal it is emitted and whatever is the velocity of the primary rays, so long as it is greater than 80 volts. These conclusions are all based on the measurement of the relation between the current from an electrode emitting the radiation and the potential difference. An examination of the curves given by Gehrts (*loc. cit.* pp. 1014, 1015) shows that they are very similar to those obtained by myself (Phil. Mag. Aug. 1911, p. 291) when measuring in a similar manner the same relation for a current carried by δ rays excited by α rays. It appears probable that the δ rays of the same quality are emitted under the action of both α and β rays.

3. It has been shown in the previous papers that the δ rays are not homogeneous in velocity and that, for this and other reasons, the relation between the current carried by them and the acting potential difference will vary somewhat with the distribution of the rays and the arrangement of the electrodes. Accordingly, in order to produce conclusive proof of the identity of the rays produced by different agents, it was necessary to ensure that they were investigated in the same conditions. It was easy to attain these conditions if the β rays which were to be compared with α rays were those excited by the action of Röntgen rays.

The apparatus used was that described in a previous paper[‡]; it consists of two parallel electrodes, one of which is pierced by a hole, covered with thin foil, through which the rays enter the space between the electrodes, in both of which they excite δ rays. Two series of experiments were conducted with the electrodes in exactly the same condition; in the first the rays were α rays proceeding from polonium placed above the hole; in the second the rays were Röntgen rays passing through the same hole. In each case the current was measured for different potential differences between the electrodes; in the former case the measurements were made by the method described already, in the latter by the usual compensation method designed to render the measurements independent of the intensity of the Röntgen rays. The largest possible error in the determination of the current for a given P.D. was 3 per cent. of the maximum current when Röntgen rays were used and 1 per cent. when α rays were used.

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[*] Lenard, *Ann. d. Phys.* viii. p. 149 (1902); xii. p. 449 (1903); xv. p. 485 (1904).

[†] Gehrts, *Ann. d. Phys.* xxxvi. p. 995 (1911).

[‡] Phil. Mag. April 1912, p. 464.

4. The Röntgen rays used were heterogeneous primary rays. No change in the measurements due to variations in the hardness of the bulb could be certainly detected. Experiments were made when the electrodes were covered with gold, copper, and paper coated with graphite. The maximum saturation current (measuring the total number of δ rays) for copper was about one half of that for gold; for the paper the current was so small that it could not be detected with certainty and was certainly not greater than 1 per cent. of that for gold. Such a result is, of course, to be expected; for the β radiation excited by Röntgen rays in gold and copper is known to be very much more intense than that excited in paper. However, whether the electrodes were covered with gold or copper, the relation between the current and the potential difference was very nearly the same. It may be concluded, therefore, that the quality of the δ rays excited by β rays, like that of the δ rays excited by α rays, is independent of the penetration of the primary rays and of the nature of the material they strike.

5. The results of the comparison of Röntgen rays with α rays are shown in the figure below. The abscissæ represent P.D.'s between the electrodes; the unit is 1·02 volts. The current was found to be completely saturated for a P.D. 40. If i_V is the current between the electrodes when one electrode is at a potential V higher than the other, the ordinates represent the values of $\frac{i_{+V}-i_{-V}}{i_{+40}-i_{-40}}$ (see the previous papers). The continuous curve represents the results obtained with Röntgen (*i. e.* β) rays; the points marked × represent the results for α rays. It will be seen that the two series of results are exactly the same for all P.D.'s greater than 2.

No significance important for our purpose can, I think, be attributed to the slight divergence of the curves for small P.D.'s*. In previous papers the uncertainties affecting this part of the curves have been fully discussed. It was found that the curves for positive and negative P.D.'s were exactly the same when Röntgen rays were used, but not when α rays were used. It was thought that the divergence might be attributed to this cause, but it was found that if the curves for α rays were made yet more asymmetrical by using as a source of those rays the active deposit of thorium on the surface of one of the electrodes in place of the polonium behind the window, no change in the form of the curve obtained by adding positive and negative values was obtained. Nevertheless I am inclined to attribute the divergence to some difference in the distribution of the δ rays, and have no hesitation in concluding that *the δ rays excited by β rays are precisely similar to those excited by α rays. The properties of the δ rays are a function neither of the properties of the ionizing rays nor of the material which they ionize; they are a function of the properties of some mechanism which is concerned in all ionization.* This conclusion appears to me of the highest importance.

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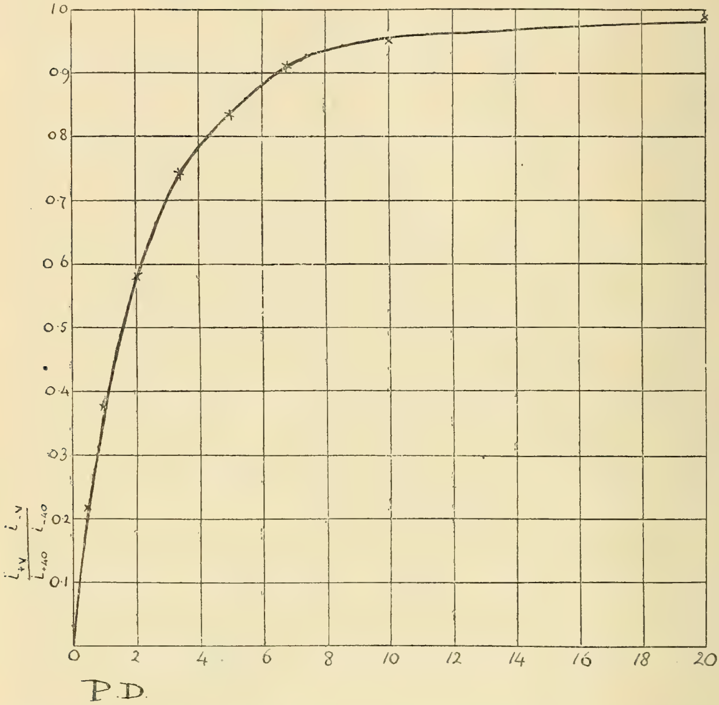
* From the figure it might not be seen that there are divergencies for small potentials; the steepness of the curve conceals errors in the ordinates. For values of V less than 1, the ordinate of the α ray curve is about 10 per cent. greater than that of the Röntgen ray curve, while for values of V greater than 2 the difference between the ordinates is never more than 1 per cent. The curve makes errors in V of equal value with errors in the ordinate, whereas experimentally the values of V are certain to 1 in 3000.



6. Perhaps it is well to remark that these experiments

have no connexion with those by which Curie and Sagnac proved that metals under the influence of Röntgen rays emit negatively charged rays of considerable penetrating power. The form of the curves obtained here is determined wholly by rays which have a velocity less than 40 volts. The secondary β rays have a velocity of several thousand volts, and they will pass from one electrode to the other practically uninfluenced by the small P.D.'s employed. Their only effect will be to produce a current independent of the P.D.'s if the number of secondary rays emitted from the two electrodes is not the same. The value of $i_{+\text{V}}-i_{-\text{V}}$ is, of course, independent of such a current.

7. Two results obtained incidentally may be mentioned. The first is not of any great importance. It has often been announced that the number of δ rays given off by a source of α rays is greater than that given off by any substance struck by the rays from that source. The experiments in which the source of α rays was the active deposit of thorium on one of the electrodes show that this announcement is erroneous. It has usually been made as a result of measurements with polonium, and the apparently greater emission from that substance is to be attributed to the entanglement of the δ rays liberated in the soot-like deposit in which the polonium is contained (see the investigations on soot-covered electrodes in Phil. Mag. Jan. 1912, p. 46, &c.).

8. The second is perhaps more important. When both electrodes were covered with paper the amount of δ rays produced from them was certainly less than 1 per cent. of that produced from the electrodes when covered with gold; but when one electrode was covered with paper and the other with gold, the amount of δ rays produced at both electrodes was approximately the same. It has been explained in the former papers why it is difficult to determine with any accuracy the respective contributions of the two electrodes to the current when they are covered with different materials. There was no evidence of any difference between the contributions of the gold and the paper electrodes, but they may have differed by as much as 30 per cent. Since the electrodes were so arranged that very nearly all the secondary β rays excited from one electrode would fall on the other, these observations would seem to show that the number of δ rays excited by a given number of β rays is (like the number of δ rays excited by a given number of α rays) almost independent of the material on which the rays fall; and they show also that the emission of δ rays is determined by the number of β rays acting, and not by the number of Röntgen rays. No δ rays

are produced from *two* paper electrodes because very few β rays are excited in the paper; but δ rays are excited from a paper electrode opposite a gold electrode because the β rays from the latter can fall on the former. This result was, of course, to be expected. The emission of δ rays from a solid is equivalent to ionization in a gas, and since there is no evidence of the production of ions by Röntgen rays, except by means of the β rays to which they give rise, it was to be expected that no δ rays should be excited in a substance by Röntgen rays except when β rays also fall on it.

Summary.

The important conclusions of this paper are given at the end of § 5 and of § 8.

Leeds University, July 1912.

LXXX. *The Construction and Constants of a Rectangular Galvanometer. By* Allan Ferguson, *B.Sc. (Lond.), Assistant Lecturer in Physics in the University College of North Wales, Bangor*[*].

Summary of Contents.

§ 1. Description.
§ 2. Constant of a 'single turn' galvanometer.
§ 3. Comparison of square and rectangle.
§ 4. Comparison of square and circle.
§ 5. Variation of field-intensity near centre of square.
§ 6. Calculation of field-intensity at points on axis of rectangle perpendicular to its plane.
§ 7. Calculation of constant of 'strip' galvanometer.
§ 8. Calculation of constant of 'single-layer' galvanometer.
§ 9. Equivalence of single layer winding and current sheet.
§ 10. Constant of 'multiple-layer' galvanometer.
§ 11. Calculation of the 'Helmholtz' condition.
§ 12. Irregularities of winding.
§ 13. Correction for inequalities in sides of frame.
§ 14. Correction for finite curvature at corners of square.
§ 15. Temperature correction.
§ 16. Experimental results.
§ 17. Conclusion.

§ 1. THE instrument described below was intended originally to afford a laboratory exercise for the verification of the relation

$$F=i\left(\frac{1}{p_1}+\frac{1}{p_2}+\frac{1}{p_3}+\frac{1}{p_4}\right), \quad \ldots \ldots \quad \text{(i.)}$$

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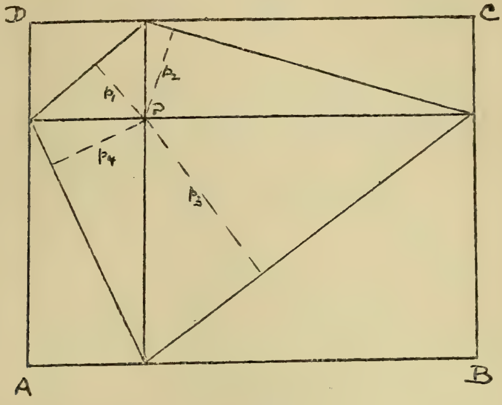
[*] Communicated by Prof. E. Taylor Jones.

giving the magnetic force at any point P in the plane of a rectangular coil carrying a current i, the perpendiculars p_1 &c. having the meaning exhibited in fig. 1.

Fig. 1.



Equation (i.), which is readily obtained by integrating Ampère's formula round the rectangle, may then be tested by placing the needle of a mirror magnetometer at some definite point in the plane of the rectangle, determining $\Sigma\frac{1}{p}$ by, say, a graphic method, and comparing it with the value of F/i obtained by means of the magnetometer and a current balance.

It seemed, however, that such a coil, used as an absolute galvanometer, possessed certain advantages, and as the writer has not seen anywhere a detailed description of such a galvanometer, a discussion of the chief points of interest connected therewith is here presented.

In all absolute instruments, the cylindrical type is chosen on account of the relative ease with which a cylindrical surface may be turned. But if the use of metallic materials is vetoed on account of the possible presence of traces of magnetic substance, the construction of a wooden bobbin which shall reduce the danger of warping to a minimum is a matter of some difficulty *. On the other hand, it is fairly easy to construct a strong wooden rectangle so that the irregularities in its surface shall be small compared with the unavoidable experimental errors introduced in reading the deflexions of the magnetometer, &c.; but it is difficult to say, *a priori*, whether such a frame will show any marked tendency to warp—such a point can only be satisfactorily tested by time. In any case the warping can be minimised by following the plan suggested by Gray for a cylindrical bobbin *.

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* Gray, 'Absolute Measurements,' vol. ii. p. 353.

The instrument under discussion consists of a horizontal baseboard provided with levelling screws, and carrying a horizontal scale on its upper surface ; in this surface are cut two grooves, along which slides a second horizontal board carrying a vertical rectangle about 60 × 40 cm. in external dimensions. Around this rectangle, which has been coated with insulating varnish, is uniformly laid a thin brass strip 1 cm. wide, the ends of the strip being bent outwards at their point of contact, and insulated from each other by a thin strip of mica ; the current is led into and out of the frame by attaching these ends to a spring clip. The magnetometer, which is of the Kelvin type and is provided with a plane mirror, is supported at the centre of the rectangle on an independent table, and by moving the rectangle in its own plane along a line parallel to the base-board scale the variations in the value of F/i, and the concomitant variations in $\Sigma \frac{1}{p}$, can readily be compared.

As described, the instrument may be put to more uses than would be the case were it primarily designed for use as a standard instrument; and, in such cases, what is gained in comprehensiveness is apt to be lost in precision. Still, the results obtained by the galvanometer in this form will serve to illustrate the points discussed below.

§ 2. If the needle be suspended at the centre of a rectangle of sides $2c$ and $2d$, the perpendiculars from the centre are all equal, and G, the magnetic force at the centre due to unit current in the coil, is given by

$$G = 4 . \frac{1}{p} = \frac{4 \sqrt{c^2 + d^2}}{cd}.$$

For a square of side $2c$,

$$G = \frac{4 \sqrt{2}}{c}.$$

§ 3. If a given length of wire has to be wound into a rectangular coil, the square is the least advantageous form, for, remembering that

$$c + d = \text{constant} \ (k),$$

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* Gray, *l. c.*

we have

$$G=\frac{4\sqrt{c^2+d^2}}{cd}=\frac{4\sqrt{\overline{k-d}^2+d^2}}{(k-d)\,d},$$

which is easily seen to be a minimum when $c=d$. To avoid cumbersome algebra, the square is chosen to illustrate several of the theorems discussed below. There is no difficulty whatever in extending the discussion to a rectangle.

§ 4. But even so, for a given length of winding the square shape is more advantageous as regards field-intensity at its centre of symmetry than the circle.

For at the centre of the circle we have

$$G=\frac{2\pi}{a}.$$

And if a wire of length $2\pi a$ be formed into a square

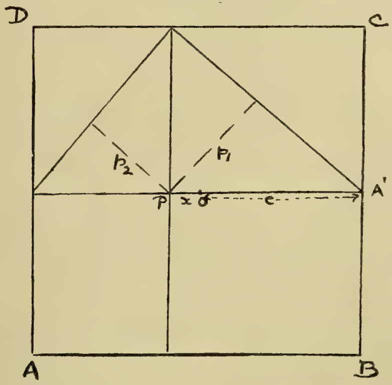
$$G'=\frac{4\sqrt{2}}{\pi a/4}=\frac{16\sqrt{2}}{\pi a},$$

giving

$$\frac{G'}{G}=\frac{16\sqrt{2}}{2\pi^2}=1{\cdot}15.$$

§ 5. It is desirable to discuss the variation in the field at points near the centre of the square, as it is, of course, necessary that the field in this neighbourhood shall be constant to the first order of small quantities.

Fig. 2.



Let us find an expression for the force at a point P on the horizontal axis of a square of side $2c$, and at a small distance x from the centre O. We have at once

$$F = 2i\left(\frac{1}{p_1} + \frac{1}{p_2}\right),$$

and

$$p_1 = \frac{c(c-x)}{\sqrt{c^2+(c-x)^2}}, \quad p_2 = \frac{c(c+x)}{\sqrt{c^2+(c+x)^2}}.$$

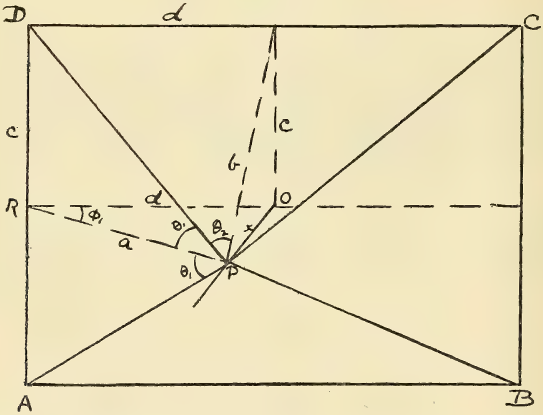
Substituting, expanding the radicals, and neglecting $\frac{x^2}{2c^2}$ and higher powers of x, we obtain

$$F_P = \frac{4\sqrt{2}i}{c}\left(1 + \frac{x^2}{2c^2}\right),$$

showing that the field is uniform over a small area near the centre if $\frac{x^2}{2c^2}$ is negligible.

§ 6. It now becomes necessary to find the magnitude of the magnetic force at a point P on a line drawn through O perpendicular to the plane of the coil.

Fig. 3.



In fig. 3, ABCD is in the plane of the paper, OP ($=x$) is perpendicular to the plane of the paper, and O is the centre of the rectangle.

The force F at P due to AD will be localised in the horizontal plane ROP as shown in fig. 4.

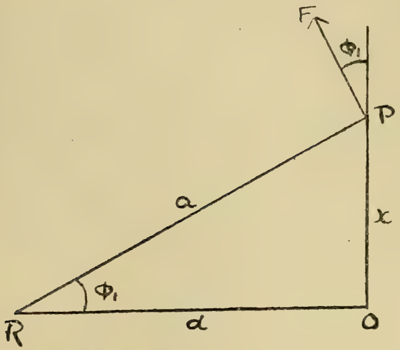
Also the total force due to AD and CB will, by symmetry, be along OP.

$$\therefore \text{ force at P due to AD} = F = \frac{2i \sin\theta_1}{a}.$$

Total force due to AD and BC

$$= 2\mathrm{F} \cos\phi_1 = \frac{4i \sin\theta_1 \cos\phi_1}{a}.$$

Fig. 4.



Hence the total force at P due to the four sides of the rectangle

$$= \mathscr{G} = 4i\left\{\frac{\sin\theta_1\cos\phi_1}{a} + \frac{\sin\theta_2\cos\phi_2}{b}\right\};$$

which, remembering that

$$\cos\phi_1 = \frac{d}{a},\ \cos\phi_2 = \frac{c}{b},\ \sin\theta_1 = \frac{c}{\sqrt{a^2+c^2}},\ \sin\theta_2 = \frac{d}{\sqrt{b^2+d^2}},$$

and $a^2 = d^2 + x^2$, $b^2 = c^2 + x^2$, gives at once

$$\mathscr{G} = \frac{4i\,cd}{\sqrt{c^2+d^2+x^2}}\left\{\frac{1}{d^2+x^2} + \frac{1}{c^2+x^2}\right\} \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

an expression which, when $x=0$, reduces as it should to the value

$$\mathscr{G} = \frac{4i}{cd}\sqrt{c^2+d^2}.$$

§ 7. This value of $\mathscr{G}$ may now be used to find the constant of the "strip" galvanometer. If the current be assumed to be uniformly distributed throughout the strip, and its value per unit breadth of the strip be i, then the force at O due to an element of the strip of breadth dx at a distance x from the central plane of the rectangle is given by

$$d\mathscr{F} = \frac{4i\,cd\,dx}{\sqrt{c^2+d^2+x^2}}\left\{\frac{1}{d^2+x^2}+\frac{1}{c^2+x^2}\right\};$$

giving

$$\mathscr{F} = \frac{4i_1}{p}\left\{\tan^{-1}\frac{pc}{a\sqrt{c^2+d^2+p^2}}+\tan^{-1}\frac{pd}{c\sqrt{c^2+d^2+p^2}}\right\},$$

where $2p$ is the breadth of the strip and i_1 $(=2pi)$ is the total current.

If we suppose that p^2 is small compared with c^2+d^2, and that the tangent may be taken equal to the angle, we have

$$\mathscr{F} = \frac{4i_1}{p}\left\{\frac{pc}{d\sqrt{c^2+d^2}}+\frac{pd}{c\sqrt{c^2+d^2}}\right\}$$
$$= \frac{4i_1}{cd}\sqrt{c^2+d^2},$$

which is the expression already obtained for a single turn of wire.

In the instrument described, $p=\cdot 5$ cm., $d=30$ cm., $c=21$ (say 20) cm., and the error introduced into the value of $\mathscr{F}$ by neglecting p^2 is easily seen to be of the order of 1 part in 10,000. The error involved in writing $\theta=\tan\theta$ in a coil of the above dimensions is also of the same magnitude.

§ 8. If the instrument is a "single-layer" galvanometer a similar argument applies, giving

$$\mathscr{F} = \frac{4iN}{p}\left\{\tan^{-1}\frac{pc}{d\sqrt{c^2+d^2+p^2}}+\tan^{-1}\frac{pd}{c\sqrt{c^2+d^2+p^2}}\right\},$$

where N is the total number of turns in the coil, and $2p$ is the over-all breadth of the winding.

§ 9. In a valuable paper on the Gray Dynamometer [*], Mr. E. B. Rosa has discussed several corrections and sources of error in a galvanometer of the single-layer type, and several of the conclusions apply, *mutatis mutandis*, to a rectangular single-coil galvanometer. In particular, the error introduced by taking the coil as equivalent to a current-sheet is carefully discussed. Without entering into further details, for reference to which Mr. Rosa's paper should be consulted, we have seen that the error involved in considering a current-sheet of breadth 1 cm. as equivalent in magnetic effect to an infinitely thin wire is of the order 1 in 10,000; and if we consider the current-sheet as formed by replacing each turn of the coil by a thin strip in breadth equal to the OVER-ALL diameter of the wire, the error is proportionately less and may be neglected. It is to be remembered, however, as a consequence of the equivalence of the coil and the current-sheet just mentioned, that the breadth $2p$ of the coil-windings is to be interpreted as meaning the total breadth of the coil measured from the *outside* of the insulation of the first turn to the *outside* of the insulation of the last turn.

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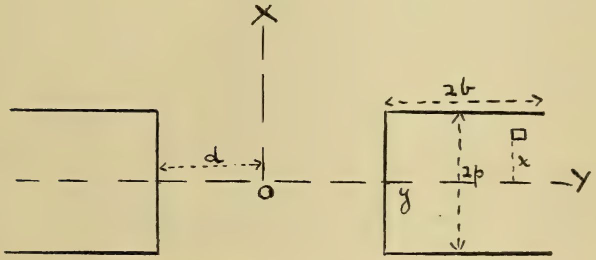
[*] Technical papers issued by the Bureau of Standards, Washington (No. 28).

§ 10. If the galvanometer be constructed of several layers of wire wound on a square frame and filling a rectangular trough of breadth $2p$ perpendicular to the plane of the coil and depth $2b$ parallel to the plane of the coil, its constant is readily calculated by methods analogous to those of § 7. Let $2d$ be the dimensions of the inner layer, as before.

Fig. 5.



Taking axes as shown in fig. 5, let $dx\,dy$ be an element of area whose coordinates are (x, y). The current through $dx\,dy$ is $in\,dx\,dy$, where n is the number of turns of wire per unit area. And the force at O due to the "elementary" square of side $2y$ is, by equation (ii.)

$$d\mathscr{F} = \frac{4in\,dx\,dy\,y^2}{\sqrt{x^2+2y^2}}\left\{\frac{2}{x^2+y^2}\right\},$$

giving

$$\mathscr{F} = 8in\int_{d}^{d+2b}\int_{-p}^{+p}\frac{y^2\,dx\,dy}{(x^2+y^2)\sqrt{x^2+2y^2}}$$

$$= 8in\,\mathrm{I}\quad\text{(say)}.$$

Hence, if N be the *total* number of turns,

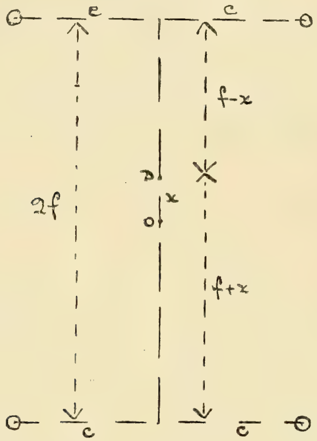
$$\mathrm{N} = 4npb$$

and $$\mathrm{G} = \frac{2\mathrm{NI}}{pb}.$$

The above problem possesses, however, more academic than practical value, as, apart from the difficulties encountered in winding such a coil, it becomes impossible to calibrate the coil in order to detect any irregularity in the windings—a matter of primary importance.

§ 11. The Helmholtz condition can also be readily worked out for, say, two square "coils" of side $2c$ with their planes at a distance $2f$ apart.

Fig. 6.



Consider the field at a point P, distant x units from O, the mid-point of the coils. We have at once, from equation (ii.),

$$\mathscr{G}_{\mathrm{P}} = 8ic^2\left\{\frac{1}{(2c^2+\overline{f-x}^2)^{\frac{1}{2}}}\cdot\frac{1}{c^2+\overline{f-x}^2}+\frac{1}{(2c^2+\overline{f+x}^2)^{\frac{1}{2}}}\cdot\frac{1}{c^2+\overline{f+x}^2}\right\}$$

$$= \frac{16ic^2}{(2c^2+f^2)^{\frac{1}{2}}(c^2+f^2)}\left\{1+\left(\frac{3f^2}{2a^2}+\frac{2f^2}{ab}+\frac{4f^2}{b^2}-\frac{1}{2a}-\frac{1}{2b}\right)x^2 + \text{terms in } x^4 \text{ \&c.} \dots\right\}$$

where, for convenience, we put

$$a = 2c^2+f^2, \quad b = c^2+f^2.$$

The condition that the coefficient of x^2 shall vanish is given by

$$6c^6-30c^4f^2-41c^2f^4-13f^6 = 0,$$

or putting $f^2 = \mathrm{X}$,

$$13\mathrm{X}^3+41c^2\mathrm{X}^2+30c^4\mathrm{X}-6c^6 = 0.$$

Solving for X, and taking the square root, we get

$$f = \phi(c),$$

where the value of the function ϕ is quite determinate. With this relation between f and c, the lowest power of x which appears in the expression for $\mathscr{F}_P$ is x^4, giving a very uniform field in the neighbourhood of O.

§ 12. A very important consideration is the error introduced through irregularities in the winding of the coils—an error which, if uncompensated, may often be of sufficient magnitude, however carefully the coils be wound, to render quite unreliable the results obtained by a single-layer galvanometer.

For this reason, any such galvanometer should be calibrated according to the method recommended by Mr. E. B. Rosa *. The method consists in dividing up the single layer into sets of 5, 10, 20, or 50 turns, according to the total number of turns in the layer and the fineness of the wire, measuring carefully the dimensions of each set of turns and calculating the magnetic force at the centre of the coil due to unit current in each set, in turn. The sum of these quantities then gives the galvanometer constant.

If the single layer be wound on a square frame of side $2c$, the expression for the force at the centre due to a turn whose plane is at a perpendicular distance x from the centre is, by equation (ii.),

$$\mathscr{F} = 8ic^2 \frac{1}{(c^2+x^2)\sqrt{2c^2+x^2}}.$$

Differentiating with respect to x, and dividing the result by $\mathscr{F}$, we obtain

$$\frac{d\mathscr{F}}{\mathscr{F}} = -\frac{x(5c^2+3x^2)\,dx}{(c^2+x^2)(2c^2+x^2)}, \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

giving the percentage error introduced into the estimation of $\mathscr{F}$ if the turn considered be displaced by an amount dx from its proper position. The percentage error introduced, as is readily seen from equation (iii.), is zero for a small displacement of the central turn, and steadily increases with x. Thus, for a square "coil" of 40 cm. side, if we assume the single layer to be wound over a length of 10 cm. perpendicular to the plane of the coil, the percentage error introduced by a displacement of, say, ·01 cm. in the last

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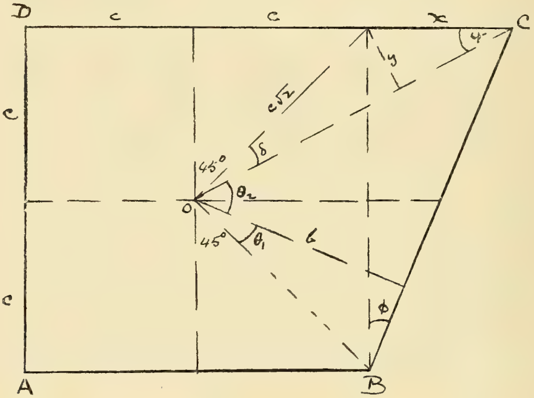
* Rosa, *l. c.*

turn is given by putting $x=5$, $c=20$, $dx=\cdot 01$ in equation (iii.) above, giving

$$\frac{d\mathscr{F}}{\mathscr{F}}=\frac{1}{3000}, \text{ approximately.}$$

§ 13. Consider now the method of correction of the value of the galvanometer constant due to the sides of the square not being quite true. We shall consider only the case in which *one* of the sides of the square is in error by an amount x. The result may be readily extended.

Fig. 7.



The force at O due to unit current in the single turn of wire ABCD

$$=\mathrm{G}=\frac{2\sin 45^\circ}{c}+\frac{2\sin 45^\circ}{c}+\frac{\sin 45^\circ}{c}$$

$$+\frac{\sin(45+\delta)}{c}+\frac{1}{b}(\sin\theta_1+\sin\theta_2)$$

$$=\frac{5}{\sqrt{2}\,.\,c}+\frac{1+\delta}{\sqrt{2}\,.\,c}+\frac{1}{b}(\sin\theta_1+\sin\theta_2). \quad . \quad . \quad . \qquad \text{(iv.)}$$

Also

$$\tan\phi=\phi=\frac{x}{2c},$$

$$\sin\delta=\delta=\frac{y}{c\sqrt{2}},$$

$$\psi=45-\delta.$$

$$\therefore \quad y=x\sin\psi=x\sin(45-\delta)=\delta c\sqrt{2},$$

giving

$$\delta=\frac{x}{2c+x}, \text{ and } \therefore \quad 1+\delta=\frac{2(c+x)}{2c+x}.$$

$$\therefore \quad \mathrm{G}=\frac{5}{c\sqrt{2}}+\frac{1}{c\sqrt{2}}\cdot\frac{2(c+x)}{2c+x}+\frac{1}{b}(\sin\theta_1+\sin\theta_2).$$

Also from fig. 7,

$$b=c\sqrt{2}\cos\theta_1=\mathrm{OC}\cos\theta_2=c\sqrt{2}\sin(45+\phi).$$

The third of these equations for b gives

$$b=c(1+\phi)=c\left(1+\frac{x}{2c}\right)=\frac{2c+x}{2},$$

and

$$\begin{aligned}\mathrm{OC}=\mathrm{OK}+\mathrm{KC}&=\mathrm{C}\sqrt{2}+x\cos\psi\\&=\mathrm{C}\sqrt{2}+x\cos(45-\delta)\\&=\mathrm{C}\sqrt{2}+\frac{x}{\sqrt{2}}(1+\delta)\\&=\mathrm{C}\sqrt{2}+\frac{x}{\sqrt{2}}\frac{2(c+x)}{2c+x}.\end{aligned}$$

Whence

$$\cos\theta_1=\frac{b}{c\sqrt{2}}=\frac{(2c+x)\sqrt{2}}{4c},$$

or

$$\sin\theta_1=\frac{1}{\sqrt{2}}\cdot\frac{2c-x}{2c},$$

and

$$\cos\theta_2=\frac{b}{\mathrm{OC}}=\frac{1}{\sqrt{2}} \text{ (to first order)};$$

$$\therefore \quad \sin\theta_2=\frac{1}{\sqrt{2}}.$$

$$\therefore \quad \frac{1}{b}(\sin\theta_1+\sin\theta_2)=\frac{4c-x}{c\sqrt{2}(2c+x)}.$$

Hence, substituting this value in equation (iv.) for G, we obtain on reduction

$$\mathrm{G}=\frac{4\sqrt{2}}{c}\left(1-\frac{3}{8}\cdot\frac{x}{c}\right).$$

Thus the force at O in fig. 7 is approximately equal in magnitude to that at the centre of a square of semi-side

$c+\frac{3}{8}x$. It appears, therefore, that, warping apart, any slight deviation from trueness in a side of the square can be readily computed and allowed for.

§ 14. We now proceed to consider the effect of the finite bending of the wire or strip at the corners of the square.

Fig. 8.

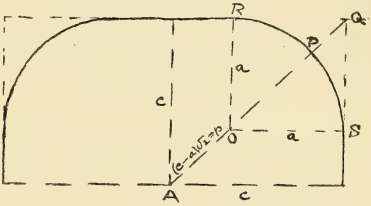
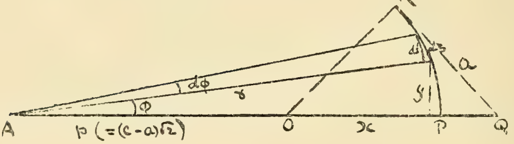


Fig. 9.



The above figures—which are drawn out of all true proportion—require no explanation. We assume the wire or strip at the corner of a square of side $2c$ to be bent into an arc of a circle of radius a, a being small compared with c. In figs. 8 and 9 above corresponding letters refer to the same points. Suppose the origin to be taken at O; then with the notation shown above, the relations

$$d\mathscr{F}=\frac{ds\sin\theta}{r^2},\quad ds'=ds\sin\theta,\quad\text{and}\quad\frac{ds'}{r}=d\phi,$$

give at once

$$\frac{d\phi}{d\mathscr{F}}=r.$$

Also, since

$$y^2+(x+p)^2=r^2,\quad x^2+y^2=a^2,$$

and

$$x+p=r\cos\phi,$$

we have

$$r=p\cos\phi\pm\sqrt{a^2-p^2\sin^2\phi},$$

or

$$d\mathscr{F} = \frac{d\phi}{p\cos\phi \pm \sqrt{a^2 - p^2\sin^2\phi}}$$

An integration sufficiently exact for our purpose may be obtained by neglecting the quantity under the radical sign. Hence

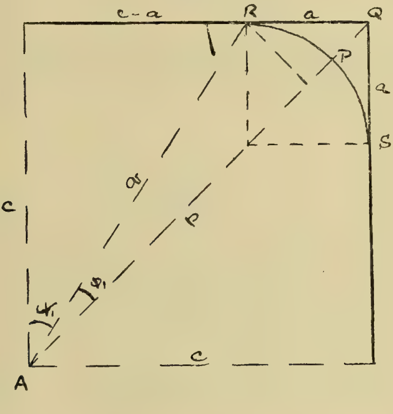
$$\mathscr{F} = \int_0^\phi \frac{d\phi}{p\cos\phi}$$

$$= \frac{2}{p}\log(\tan\phi_1 + \sec\phi_1)$$

$$= \frac{2}{(c-a)\sqrt{2}}\log\left(\frac{2\sqrt{c}\sqrt{c-a}+a}{2c-a}\right),$$

substituting the values of tan ϕ_1 and sec ϕ_1 from fig. 10.

Fig. 10.



Putting $a = kc$, and neglecting squares of k,

$$\mathscr{F} = \frac{2}{c(1-k)\sqrt{2}}\log\left\{\frac{2\sqrt{1-k}+k}{2-k}\right\}$$

$$= \frac{2}{c(1-k)\sqrt{2}}\log\left\{1 + \frac{k}{2}\right\}$$

$$= \frac{k}{(1-k)c\sqrt{2}}.$$

This expression, then, gives the force at the centre of the square due to the quadrant RPS. The force due to the two linear elements RQ, QS, is (fig. 10) easily seen to be given by

$$\mathrm{F}' = \frac{2\sin(\psi+\phi)}{c} - \frac{2\sin\psi}{c}$$

$$= \frac{2}{\sqrt{2}c} - \frac{2(c-a)}{qc}$$

$$= \frac{2}{\sqrt{2}c} - \frac{2(c-a)}{c\sqrt{2c}\sqrt{c-a}}$$

$$= \frac{\sqrt{2}}{c}\left(1 - \sqrt{\frac{c-a}{a}}\right)$$

$$= \frac{\sqrt{2}}{c} \cdot \frac{1}{2}\frac{a}{c} = \frac{k}{c\sqrt{2}}.$$

Hence

$$\mathscr{F}' = \mathscr{F}(1-k).$$

For the case of a single turn of wire wound on a square of semi-side 20 cm., if we assume as an outside value $a=1$ mm., then $k=\frac{1}{200}$, and

$$\mathscr{F}' = \frac{199}{200}\mathscr{F},$$

whence it easily follows that the error in the estimation of the galvanometer constant due to the curvature at the corners in this case amounts to less than one part in half-a-million, and is therefore quite negligible.

§ 15. It remains to consider the effect of temperature changes on the value of the galvanometer constant. If we assume

$$\mathrm{G} = \mathrm{G}_0(1+\beta t),$$

then β may be defined as the increase in the value of the galvanometer constant per unit field per unit rise in temperature, due to the increase in dimensions of the rectangle. Therefore, if α be the linear coefficient of expansion of the material of the rectangle, we have

$$\mathrm{G}_0 = \frac{4\sqrt{c_0^2+d_0^2}}{c_0 d_0},$$

and

$$G = G_0(1+\beta t) = \frac{4\sqrt{c^2+d^2}}{cd}$$

$$= \frac{4\sqrt{c_0{}^2(1+\alpha t)^2+d_0{}^2(1+\alpha t)^2}}{c_0 d_0(1+\alpha t)} = \frac{G_0}{1+\alpha t}$$

$$= G_0(1-\alpha t),$$

whence $\beta = -\alpha$.

§ 17. To test the performance of the galvanometer, a determination of H was made by its aid, and the value so obtained was compared with that given by the Helmholtz coils of a cylindrical galvanometer of the type described in Gray's 'Absolute Measurements,' vol. ii. p. 353. All necessary precautions were taken, the constants of the two galvanometers being determined by measurements which in all cases were referred to a standard metre scale, and the current balances used being carefully compared with each other.

As the measurements involved present no particular novelty, the results only are given.

I. Helmholtz Galvanometer, cylindrical coils.

Constant of galvanometer = 1·85705.

Values of H:—

·17203, ·17212, ·17208, ·17217, ·17201, ·17181, ·17176,
·17183, ·17165, ·17171, ·17141, ·17145, ·17147, ·17121,
·17157, ·17156, ·17148, ·17146, ·17139.

Mean H = ·17164 C.G.S. units.

II. Rectangular Galvanometer.

Galvanometer constant = ·231085.

Values of H:—

·17205, ·17129, ·17168, ·17144, ·17147, ·17097, ·17180,
·17207, ·17223, ·17239, ·17116, ·17187, ·17215, ·17164,
·17170, ·17234.

Mean H = ·17177 C.G.S. units.

The agreement between the two results represents about the limit of accuracy in reading the current balances. Moreover, no account has been taken of the diurnal variations in H, which would sensibly affect the fifth decimal place.

§ 17. It seems, therefore, that the simple instrument described above shows roughly the same order of accuracy as the standard cylindrical coil. It is simple in construction and use, reliable in results, whilst it possesses two main outstanding advantages :—For a given length of winding it is more sensitive than the circular form, and any departure from trueness in form can be readily and exactly allowed for.

The writer's thanks are due, and are tendered, to Professor E. Taylor Jones, whose help and counsel have been continually placed at his disposal ; and to Mr. J. A. Hughes, B.Sc., who has given valuable assistance in recording and reducing the observations detailed in the last section.

University College of North Wales, Bangor.
June 1912.

(*Note added October* 1912.) Since writing the above, two interesting papers* by W. Wien and H. Kahle have come before the writer's notice. The papers describe a dynamometer, one of the coils of which is rectangular in section. Some of the results given above are there discussed, but the overlapping is not serious, whilst the methods of attacking the problem differ from those in the present paper.

LXXXI. *On Magnetic Rays in Different Gases.*

By A. Righi, *Professor of Physics, University of Bologna* [†].

I PRESENT in this note some observations on a paper lately published [‡], in which Messrs. L. T. More and E. R. Rieman give an account of some experiments concerning the magnetic rays.

As is known, my researches were always made with tubes containing rarefied air ; and the two authors, repeating them, have confirmed entirely my results, including the disappearance (first noted by me) of the magnetic rays when the magnetic field becomes too intense [§]. They have, on the other hand, in some cases obtained different results by introducing other gases into the tubes in place of air ; and hence they find reason, if not to contest, at least to throw some doubt on the theory proposed by me to explain the phenomena presented by the magnetic rays.

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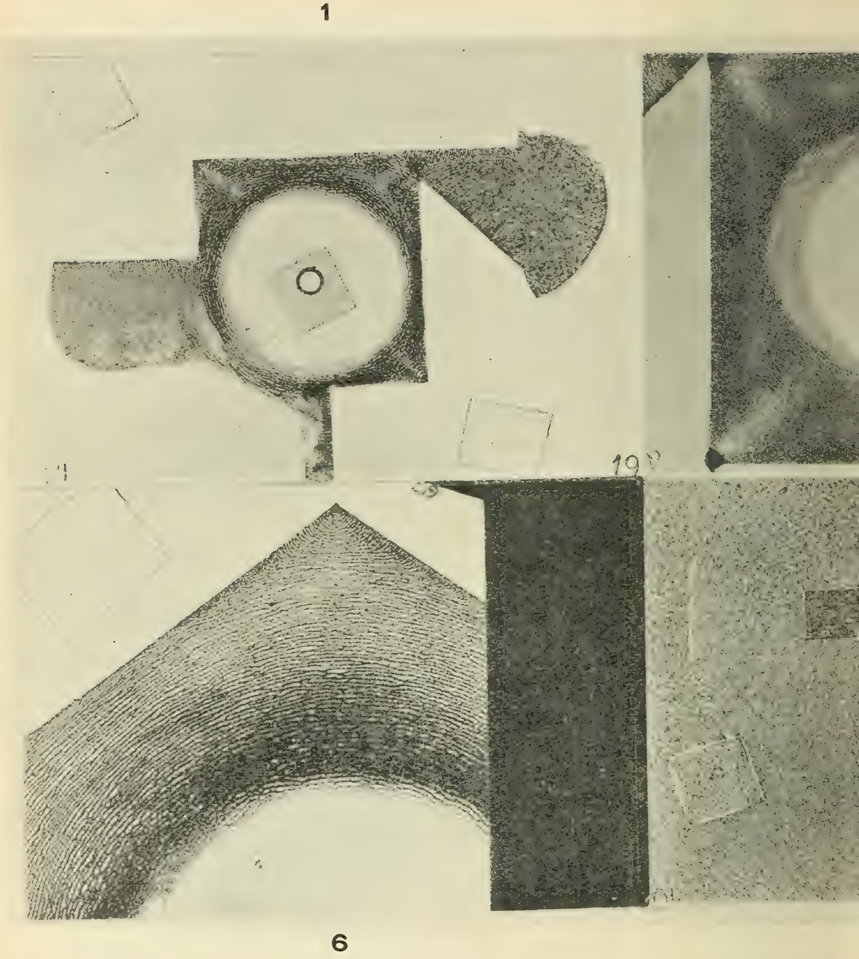
[*] Wied. *Ann.* 1896, vol. lix.

[†] Communicated by the Author.

[‡] Phil. Mag. No. 140, p. 307.

[§] *Loc. cit.* p. 312.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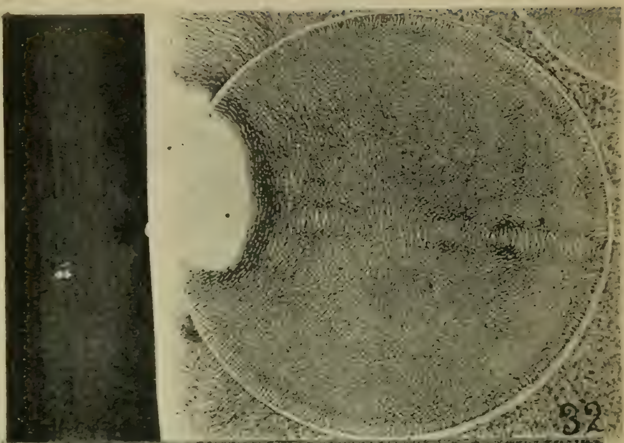

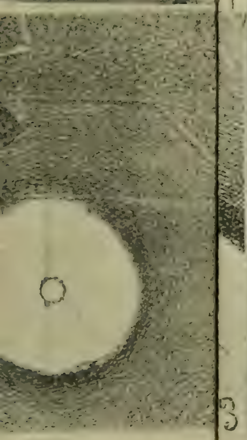

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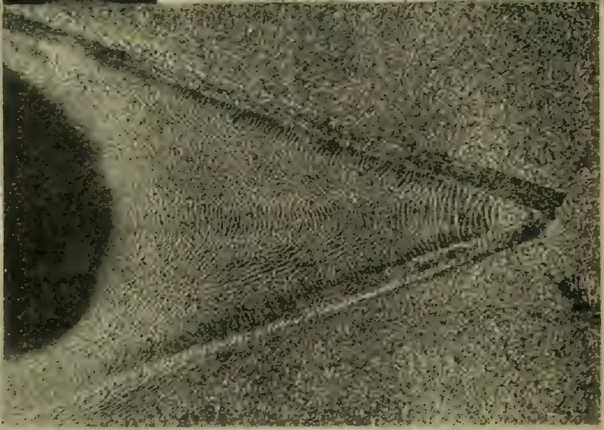

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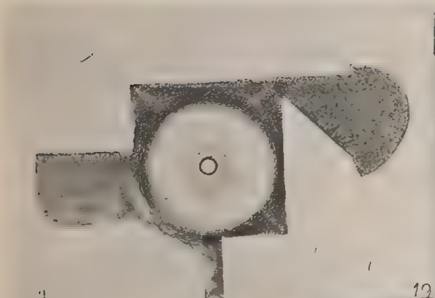

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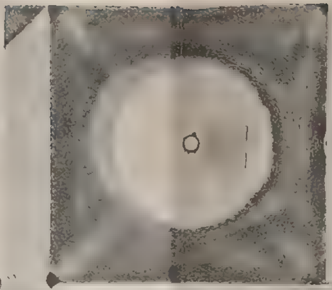

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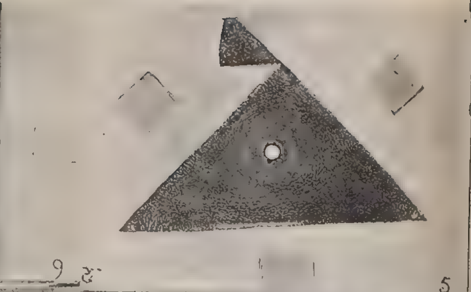

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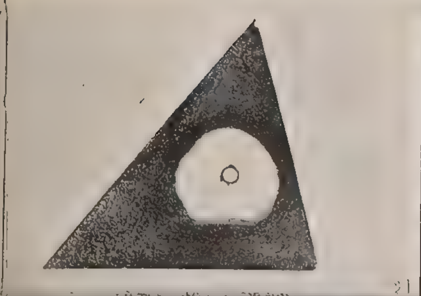

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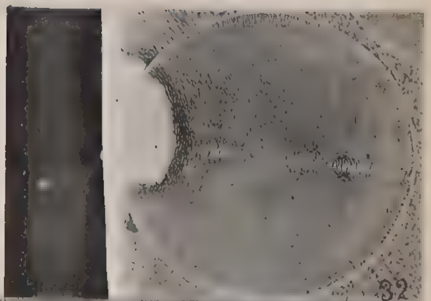

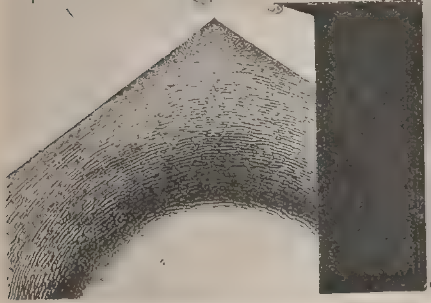

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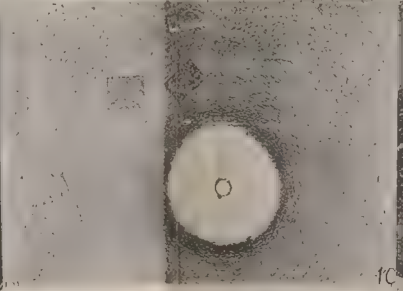

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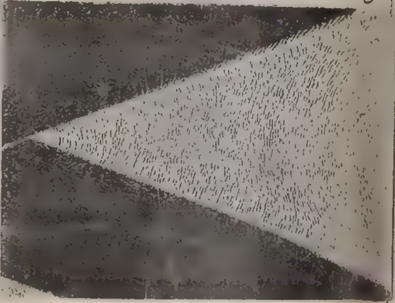

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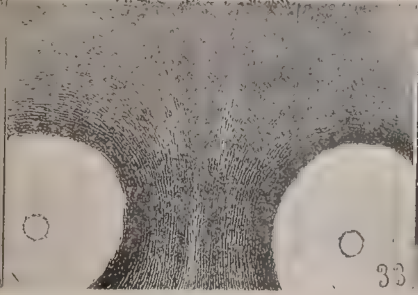

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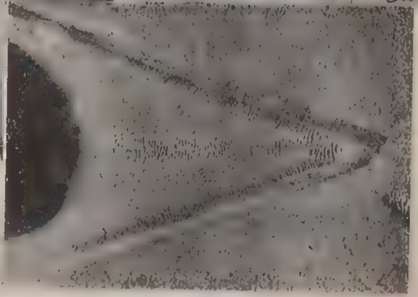

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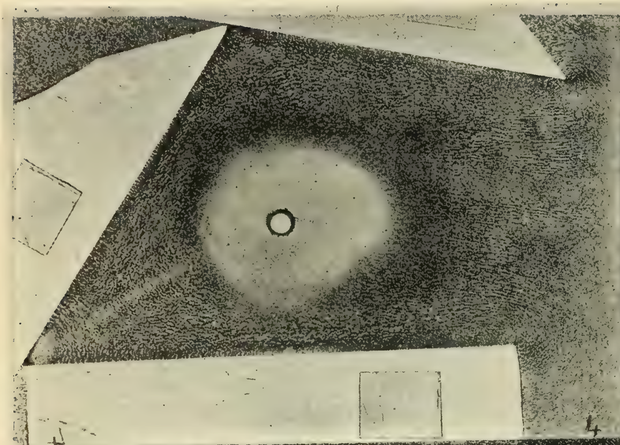

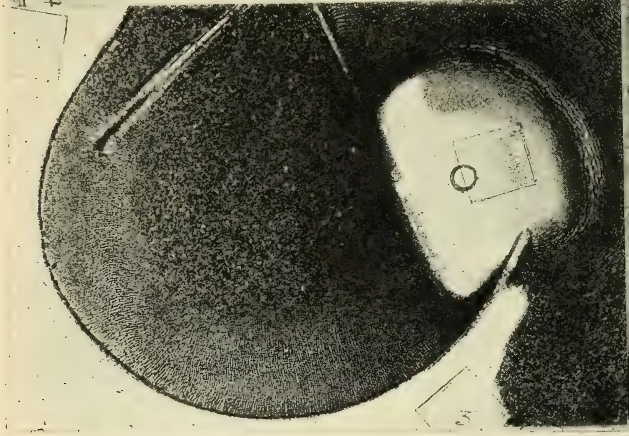

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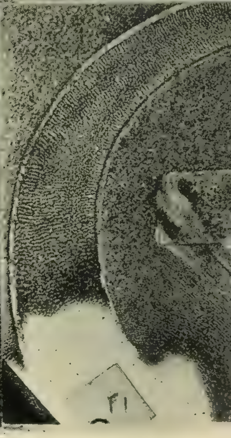

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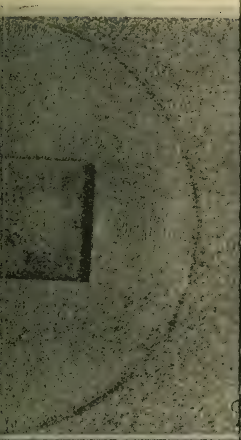

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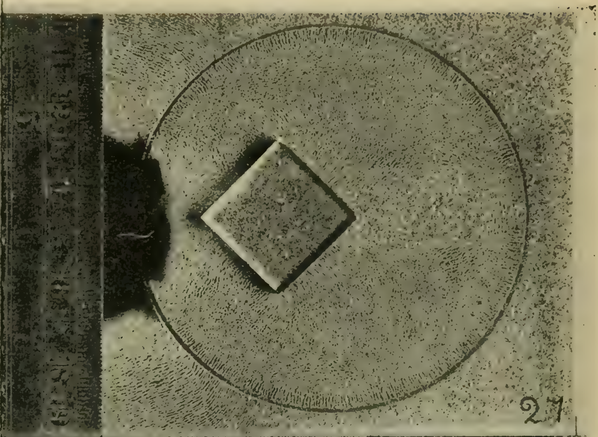

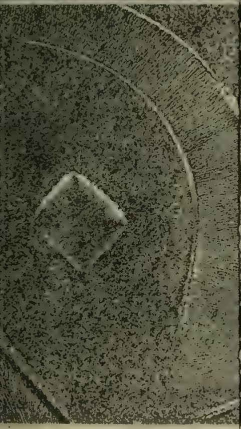

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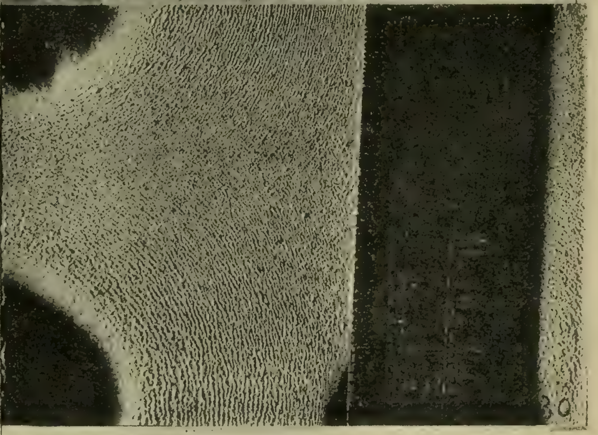

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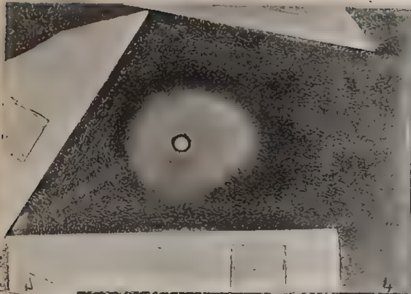

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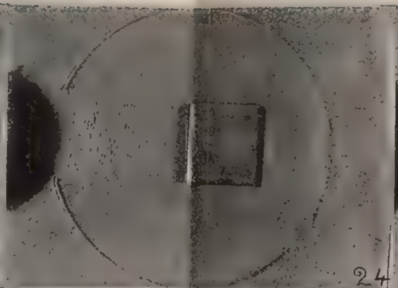

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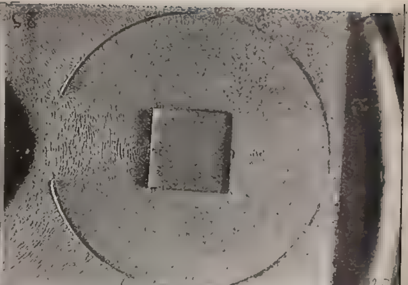

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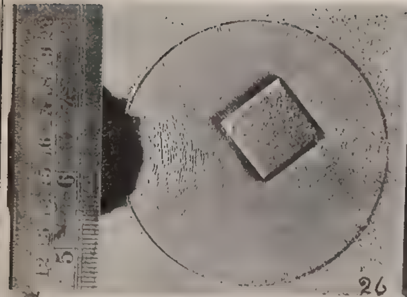

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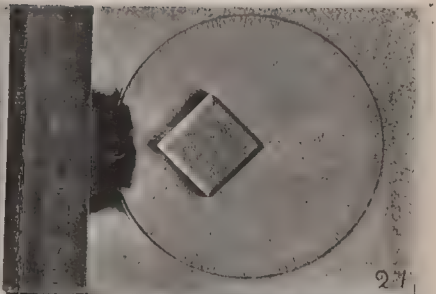

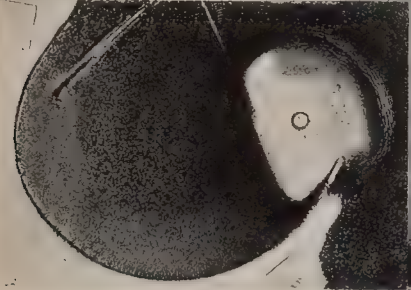

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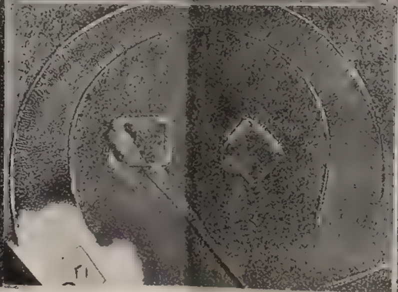

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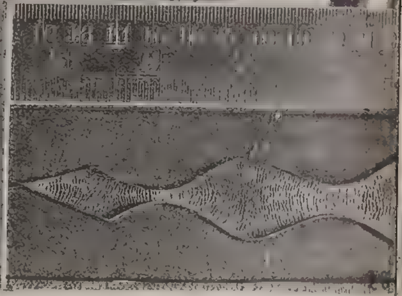

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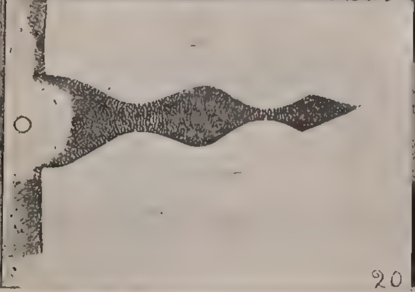

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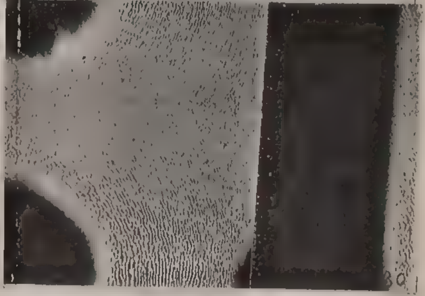

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My long experimental researches on these phenomena induced me :

(1) To abandon as absolutely insufficient the usual explanation, according to which the action of the field would be limited to altering the path followed by the electrons ;

(2) To assume that, in addition to such an alteration of path, the magnetic field would cause some electrons to join with positive ions, so as to give rise to systems analogous to the system formed by a planet and its satellite.

This hypothesis is justified particularly by considering, that the great instability of such systems (whose destruction is evidently more easy than the ionization of an atom) is diminished by the magnetic field for those in which the electron revolves in a determinate sense, and besides, that such systems as are made less unstable by the field, must be formed preferably under the action of the magnetic force.

This hypothesis has been always presented by me as plausible and worthy to be taken into consideration; but I did not conceal the necessity and the hope of a future elaboration that will make it able to explain also some phenomena still obscure in detail. Considering that Messrs. More and Rieman, after having reviewed my theory, say, that it *is simple, plausible, and accounts for most of the observed phenomena* *, I can limit myself to a few considerations on some other points of their Note.

It is specially my experiments, which demonstrate the formation of a luminous column, placed in the prolongation of the magnetic rays and perfectly distinct from them (for sake of brevity I will adopt the denomination of *induced* column, proposed by the authors) that they have repeated at first, and then varied.

According to my theory this column of light would be due to the periodical discharge of the cloud of positive ions given up by the magnetic rays where, the intensity of the magnetic field being too much reduced, the pairs ion-electron cease to exist. I called the region of the gas in which these ions accumulate the *virtual anode.* As to the periodicity pointed out, it depends on the fact, ascertained by me, that the magnetic field causes the discharge, and of course the phenomena of the magnetic rays, to be discontinuous or intermitting. As the existence of the virtual anode cannot be easily explained otherwise, the said experiment constitutes a confirmation of my theory.

The authors did not observe the induced column when they substituted certain other gases for the air in my discharge-tubes. But in my opinion that does not at all constitute an objection against my explanation ; it would show only the necessity for completing the fundamental hypothesis, or at least for finding the reason why in certain gases the formation of the virtual anode does not take place to a perceptible degree.

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* *L. c.* p. 311.

Considering also that in air the magnetic rays are produced only in certain conditions of experiment, and particularly with a given tube only between certain limits of the pressure of the air, of the intensity of the field, and of the intensity of the discharge current, before asserting that in some gases the virtual anode does not exist, it was needful for the authors to vary these factors. As unfortunately they do not give numerical values, there remains the possibility that the absence of the virtual anode is due only to their not having combined rightly the conditions required for its production.

However, I admit willingly the facts asserted, which appear to me very interesting from the circumstance that, according to the authors, mixtures of nitrogen with one of the three gases, oxygen, hydrogen, and carbon dioxide, act in the same manner as air, while the induced column is absent with the natural illuminating gas (first experimented with by them), and also with the pure gases above mentioned. In effect this singularity of nitrogen could be paralleled by another one presented by the same gas, which is almost the only one (carbon monoxide shows less markedly the same behaviour) in which the phenomenon of the *globular discharge*, already described and studied by me, is produced.

Speaking of the virtual anode I must also remark, that the authors have given to one of the facts observed by them (which coincides with one already described by me, though this appears to have escaped their attention) a not rigorous interpretation. In certain gases they observed the production of the induced column, but of small length, and besides ascertained that it was always bent in the same sense (showing that it was due to a positive current directed from the extremity of the magnetic rays to the bottom of the discharge-tube), whatever the region of the column to which the lateral magnetic pole was approached. From that the authors rightly infer, that in such a case the virtual anode *with a positive current directed in the two senses* does not exist *; but the way in which this conclusion is presented might lead to the inference that the anode does not exist at all, and that this is an objection against my hypothesis. Instead, in this case it happens plainly, that the virtual anode is formed at the extremity of the magnetic rays, as I showed to happen, and as must happen, also with air, when the intensity of the magnetic field is relatively feeble.

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* *L. c.* p. 314.

It cannot be thought surprising if for the moment we cannot explain satisfactorily the fact, that only in some gases is the induced column produced, since the mechanism of the discharge is still imperfectly known, even when we neglect the action of the field. We shall probably attain such explanation when new experimental results have been accumulated. But there is a research which ought to have been initiated directly before formulating doubts or objections; that of examining if the marked intermittency produced in the discharge by the magnetic field when the tube contains air (which intermittency is strictly connected with the formation of the virtual anode) is produced or not with those gases in which the induced column was not observed by the authors. Evidently if, for any reason whatever known or unknown, the periodicity did not exist, the want of the induced column would be the natural consequence.

Wanting still this information, the assertion: "*It is difficult to see why the existence of this virtual anode should depend on the gas*"[*] is too absolute; and so also is the other one expressed by the authors in the following terms: "*That the gas used in the tube should have such an influence on the nature of the magnetic rays is most difficult to explain by Professor Righi's hypothesis*"[†].

But it is not at all difficult to understand, on the ground of the following considerations, that the nature of the gas, and consequently the nature of the positive ions existing in it, has a notable influence on the formation of the neutral systems ion-electron and on their behaviour.

In order that an electron may be captured by a positive ion and form with it one of those systems, it is necessary that the relative velocity of the electron (or its absolute velocity, if for simplicity the ion is considered at rest) should be smaller than a certain value. In fact, in order that the forces acting on the electron may be supposed reduced sensibly to the electrostatic force only, it is necessary that in its orbital motion round the ion, the electron remains at a distance sufficiently great from it. If such condition was not satisfied, the motion of the electron would be influenced in a notable manner also by the electromagnetic forces due

[*] *L. c.* p. 315.
[†] *L. c.* p. 313.

to the moving electrons contained in the structure of the ion; and beside it could easily happen that the electron satellite would enter in the said structure, and so the neutral atom might reconstitute itself.

For instance, taking 10^{-8} as the order of size of the lineal dimensions of an ion, it will be convenient to admit the average radius of the orbit of the electron as at least equal to 10^{-6}*. With this value, and with the values admitted for the charge and the mass of the electron, we find that the velocity of the satellite must not surpass 222 kilometres per second †.

On the other hand, the said velocity must not be too small, else the electron assumes so wide an orbit round the ion, that the instability of the system becomes excessive, considering the extreme facility with which the electron can be removed and separated from the ion. Such a degree of stability of the pairs ion-electron consistent with the manifestation of the phenomena that are supposed to be due to them, requires then that the orbit of the electrons have a radius neither too small nor too great, and therefore that the velocity of the satellite has a value comprised within certain limits.

Now it is evident that, according to the conditions in which the discharge is produced, the average value of the velocity of the electrons will be different, and therefore the number of those whose velocity is comprised in the limits above mentioned will be different. These limits depend on the nature of the ions, and particularly on their dimensions; therefore the probability of the formation of the planetary systems ion-electron, their stability, and the effect of the magnetic field upon them, may vary with the nature of the gas.

If, for instance in an extreme case, it happens that the distance between the two elements of the systems is in the majority not great enough in comparison with the size of the ions, the systems will cease to exist, not by separation, but by formation of neutral atoms. In such a case evidently the positive ions abandoned by the magnetic rays will be absent, or will exist in very small quantity, and the virtual anode will not be observed.

To conclude, the negative results of some of the experiments of Messrs. More and Rieman do not justify the supposition that my hypothesis is by its nature unfit to give in a future, perhaps very near, a satisfactory and perfect explanation of the phenomena. I may add, that the influence of the nature of the gas on the magnetic rays put in evidence by them, which cannot be at all understood in the light of the ordinary explanation, would suffice alone to prove the insufficiency of the explanation itself, and thus confirm the necessity for a new theory such as that which I have proposed.

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* Mem. of the R. Acad. of Bologna, ser. 6, t. vi. p. 7 (1909–10).

† We deduce, that the slower cathode rays must contribute above all to form the magnetic rays; or rather those electrons with velocities relatively small which, if the field did not exist, would not manifest perhaps in a perceptible manner the characters of true cathodic rays, these being constituted by electrons moving with much greater velocity.

Bologna, September 1912.

LXXXII. *Behaviour of Metallic Vapours in Flames.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper on "The Behaviour of Metallic Vapours in Flames," recently published in the Philosophical Magazine (July 1912, p. 15) I proposed to investigate the variation of the conductivity and the luminosity in a salted flame decolorized by chlorine when the electrodes used for measuring the conductivity do not stand in the metallic vapour (p. 23), anticipating that in this case the two quantities would vary together, and that the result of Smithells, Dawson, and Wilson on this subject [*] was due to the fact that their electrodes stood in the body of the vapour. A paper by Tufts in the *Physikalische Zeitschrift* has just come to my notice, describing the experiment I proposed in a slightly modified form, and giving as the result of it that in this case the luminosity and conductivity are indeed diminished in the same ratio by the introduction of chlorine. This strongly confirms the view put forward by Professor Lenard [†] and the author [‡], that the light-emission is essentially connected with the presence of free metal atoms and electrons liberated from them, it being the mutual impact of these *free* metallic atoms which is mainly, at any rate, responsible for the production of the free electrons. The conductivity in the experiment just mentioned will also be due to these electrons. The conductivity in the case where the electrodes stand in the vapour itself must be almost entirely due to surface ionization [§], accounted for by the assumption that the impact of chloride molecules with the glowing platinum is capable of liberating electrons from the platinum atoms.

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[*] That chlorine can destroy the luminosity of the vapour without much influencing the conductivity.

[†] *Sitzungsberichte der Heidelberger Academie*, Dec. 1911. "Ueber die Elektricitätsleitung und Lichtemission metallhaltiger Flammen."

[‡] *Loc. cit.*

[§] *Cf. loc. cit.* p. 18, and fig. 1.

Precisely how the light-emission depends upon the liberation and return of the electron, whether it takes place on the return only*, or also at other stages of the path of the metallic atoms in their free state, awaits further experiment.

I am, Gentlemen,
Yours faithfully,
E. N. da C. Andrade.

University College, London,
Oct. 6, 1912.

LXXXIII. *Notices respecting New Books.*

Ferguson's Percentage Unit of Angular Measurement, with Logarithms; also a Description of his Percentage Theodolite and Percentage Compass. By John Coleman Ferguson. Longmans, Green & Co.: London, 1912.

THE fundamental idea is to measure angles not by equal increments of arc, but by equal increments of the tangents of the arcs. The tangent of 45° is divided into 100 equal parts; and the radial projection of these subdivisions on the corresponding circular arc gives the graduation on the circular rim. Graduations begin at the cardinal points, N, S, E, W, pass round in both directions, and meet half-way in each quadrant. The method of subdivision is familiar in quadrant galvanometers; but it has never before been applied to surveying. There is no doubt that many operations are greatly simplified by the use of this method of graduation. The tables of logarithmic sines, cosines, tangents, and secants differ from ordinary tables in having as the argument the natural tangent instead of the arc.

LXXXIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 207.]

December 20th, 1911.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Glacial Sections at Sudbury (Suffolk).' By the Rev. Edwin Hill, M.A., F.G.S.

The sections round Sudbury were described in two Geological Survey Memoirs: since the date of publication of these much more has been disclosed. A list is given of the principal sections now existing, with references to the descriptions in the Survey Memoirs and notes of those that are there undescribed.

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* As Lenard has shown to be the case for the luminous "centres" in phosphors.

The paper gives an account of a series of sands and silts, which lie at about 200 O.D. on each side of the present Stour Valley. They seem to indicate shallow-water conditions at a level more than 100 feet above the present valley-floor.

On the silts lies Chalky Boulder Clay. The transition from silt to clay is continuous, and seems to show that, here, the transition from formation of silt to formation of Boulder Clay was a continuous transition. The undisturbed condition of the beds indicates that during this transition there was no action of thrust or drag.

At lower levels, from 180 O.D. down to 100 O.D., on the flanks of the valley lie coarse gravels and sands, with current-bedding, which point to torrential water-action. Among these occur displaced masses of previously-formed Boulder Clay, some. contorted—as if by slip down slopes. At Little Cornard brickworks there is associated with current-bedded gravels a clay, in which are embedded very large masses of remade Chalk.

The deduction from these facts is that at Sudbury, Boulder Clay began to be formed where there was quiet water, which stood on both sides of the valley at a level of over 120 feet above the present floor: and that, after such Clay had been formed, there came to be strong currents into or along the valley, at various lower levels.

These deductions agree with the probable course of events, if a submergence preceded the Chalky Boulder Clay and an emergence followed it.

2. 'The Ordovician and Silurian Rocks of the Kilbride Peninsula (County Mayo).' By Charles Irving Gardiner, M.A., F.G.S., and Prof. Sidney Hugh Reynolds, M.A., F.G.S.

The Kilbride peninsula includes three principal groups of rocks. The northern and western part is, in the main, composed of igneous rocks, contemporaneous and intrusive, of Arenig age; the southern and eastern part principally consists of Silurian rocks, but these are in the south-eastern corner of the peninsula faulted against an area of gneiss. The Arenig rocks resemble the Mount Partry Beds of the Tourmakeady and Glensaul districts—in the fact that they include cherts and shaly beds with *Didymograptus extensus*, and in the presence of gritty tuffs and coarse breccias, the latter rocks showing a magnificent development. No coarse conglomerates, however, occur, and no limestone-breccias or other representatives of the Shangort Beds of Tourmakeady and Glensaul, while Arenig sediments of all kinds are very scarce. The most interesting feature of the Arenig rocks is the great development of spilitic lavas, which are commonly associated with cherts and often show good pillow-structure. Their resemblance to the similar rock of the Girvan district is very close. An enormous mass of felsite with large quartz-phenocrysts, and often albite, as also pseudomorphs after rhombic pyroxene, occupies much of the northern part of the peninsula. There is no doubt that it, like the similar masses of Tourmakeady and Glensaul, is of Arenig date. The Silurian rocks consist principally of grits, sandstones, and calcareous flags, and dip with great regularity in directions varying from south to east. The calcareous flags (Finny School Beds) are highly fossiliferous, and have yielded over fifty species, principally of corals and brachiopods, which prove the beds to be of Llandovery age. Ill-preserved specimens of *Monograptus vomerinus*, found in the highest Silurian strata exposed, show that these are of Wenlock age.

Probably in early post-Silurian times occurred the intrusions of keratophyre and labradorite-porphyrite which are met with at, or near, the base of the Silurian. Then followed a period of important earth-movement, connected in all probability with the Caledonian movements in other regions. The area was folded into a syncline, the axis of which ran roughly north-east and south-west; and, perhaps owing to the rigid mass of felsite in the northern part of the peninsula, the Silurian rocks in adjusting themselves became traversed by numerous cross-faults. At some later period, intrusions took place of numerous small dykes and sills of dolerite.

LXXXV. *Intelligence and Miscellaneous Articles.*

SOME APPLICATIONS OF THE ELECTRON THEORY OF MATTER. CORRECTIONS. BY O. W. RICHARDSON, PROFESSOR OF PHYSICS, PRINCETON UNIVERSITY.

I REGRET that in looking over the proofs of the above paper* I failed to observe a number of errata. As these are sufficiently numerous to confuse the reader in places, I wish to indicate the following corrections:—

P. 596. Equation (3). For df read $d\psi$ and for $X\frac{\partial f}{\partial x}$ read $X\frac{\partial f}{\partial -}$.
P. 597. In the line above equation (4) read K for k in the denominator of the fraction.
P. 598. In the line below equation (8), for k read T.
P. 599. Line 9. *For* measuring *read* meaning.
P. 610. In the line above equation (35), *for* (3) *read* (28 *b*).
In the line below equation (35), *for* (10) *read* (34).
In the line above equation (37), *for* (9) *read* (33).
P. 611. Line 6. *For* (14) *read* (36).
P. 612. Line 15. *For* (17) *read* (39) and *for* (21) *read* (40).
Line 21. *For* (23) *read* (42) and *for* (22) *read* (41).
P. 613. Equation (45). For $\int_{n_1} \log\frac{dn}{d\tau}\,dn$ read $\theta\frac{\partial}{\partial\vartheta}\int_{n_1}\log\frac{dn}{d\tau}\,dn$.
P. 615. Line 9. *For* (37) *read* (47). Line 16. *For* (38) *read* (48).

* Phil. Mag. vol. xxiii. p. 594 (1912).

FIG. 1.

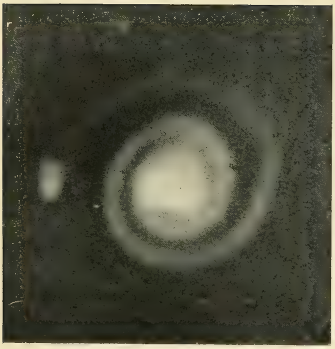


FIG. 2.

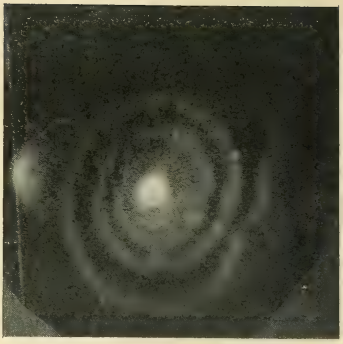


FIG. 5.

FIG. 6.

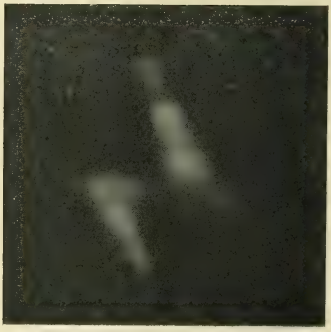


FIG. 9.

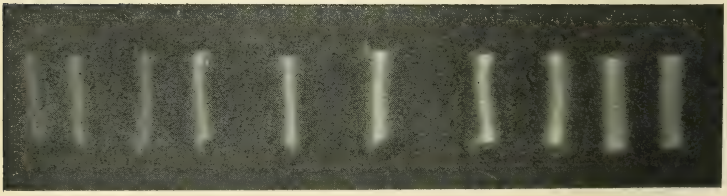


Fig. 3.

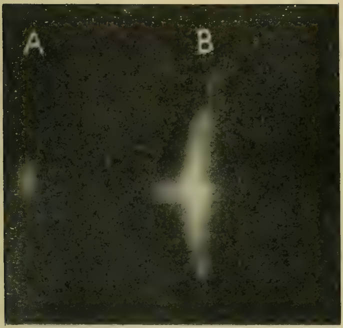


Fig. 4.

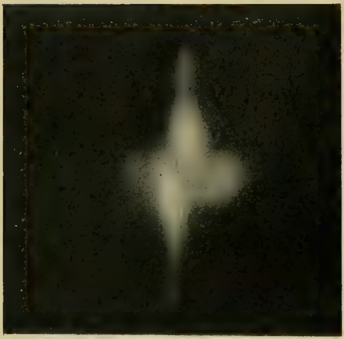


Fig. 7.

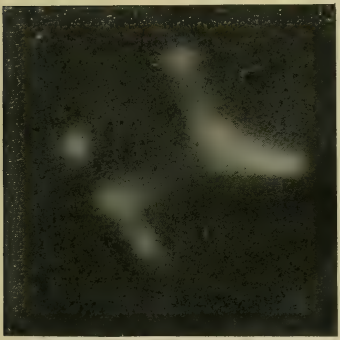


Fig. 8.

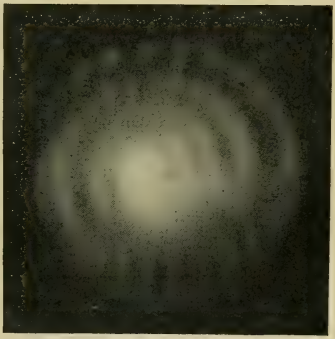
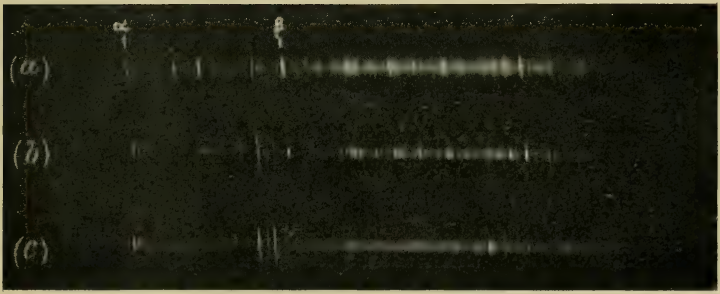


Fig 10.



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DECEMBER 1912.

LXXXVI. *The Effect of Magnetic Fields on Resistance.*—II. *By* C. W. HEAPS, *Experimental Science Fellow, Princeton University*[*].

[Plate XXIII.]

THE former paper on this subject[†] described experiments on the resistance of iron, nickel, cadmium, and Heusler alloy in both transverse and longitudinal magnetic fields. It was there shown that for cadmium (the only metal examined which was not ferromagnetic) the transverse effect was larger than the longitudinal. For the ferromagnetic metals the reverse seems to be the case, though when a large enough transverse field is used there is always a decrease of resistance in these substances[‡]. The experiments to be described were made in order to see whether it is a general rule in all para- and diamagnetic metals for a transverse field to produce a greater effect than a longitudinal; and as the internal structure of metals is more or less crystalline in nature it was thought that the study of a few natural crystals might be interesting from this view-point.

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[*] Communicated by Prof. E. P. Adams.

[†] Phil. Mag. xxii. p. 900 (1911).

[‡] It should have been mentioned that the resistance of iron in small transverse fields was also measured using a solenoid and carefully adjusted specimen, so that there seems to be no ground for Baedeker's suggestion (*Elektrischen Erscheinungen in Metallischen Leitern*) that this increase of resistance is caused by a longitudinal component of magnetization.

The apparatus used was the same as described in the former paper, but as the non-uniformity of the field of the electromagnet has been examined quantitatively there, by comparison with the field of a solenoid, no attempt has been made to allow for this error in the present experiments. In any case it is too small to cause very serious trouble. The electromagnet with poles four centimetres in diameter and two centimetres apart has been used throughout for producing the magnetic fields. Using a bismuth spiral in the first instance to measure the fields, a curve was plotted between current and field strength, so that knowing the current through the electromagnet at any time, the corresponding field could be read off from the curve.

The tellurium (from Kahlbaum) used in the experiment was cast in cylindrical form, so that for this substance the crystalline structure was especially pronounced. The small needle-like crystals could be seen radiating like spokes from the axis of the cylinder. Zinc (Kahlbaum) and gold (Johnson, Matthey & Sons) were used in the form of wire.

The natural crystals examined had in general a fairly high specific resistance, so that small bars cut out with a diamond saw could be tested very easily. The chief difficulty lay in making electrical connexions with the bars. Streintz and Wellik* conclude from their experiments that because of imperfect contact it is extremely difficult to measure the resistance of crystals. Königsberger †, on the other hand, says that if proper precautions are taken this contact resistance can be made exceedingly small—errors caused by it should be no greater than one to five per cent. He used pressure contacts and connexions soldered on copper plating. The latter method was tried and in most cases found to be the better. For bars of lead sulphide, soft tinfoil held firmly by springs against the end made a fairly good contact, but the following method was hit upon as most satisfactory. A small pit was made in a piece of copper and filled with soft bismuth solder. The end of the galenite rod was immersed in the melted solder, and when cool the expanded solder clamped the rod very securely. The presence of contact resistance was easily discovered from the behaviour of the galvanometer when the Wheatstone bridge was in balance. Ordinarily, temperature changes caused a slow and steady drift of the galvanometer, but when a poor contact was made with the specimen the drift was not steady. Waverings and sudden jumps occurred, and often when a lead was touched or moved slightly, the galvanometer flew off the scale. Repeated settings of the contacts were made until this difficulty disappeared, when the resistance always had an approximately constant value. Most of the crystals were free from troublesome cracks and fissures ; in cutting out the bars the best part of the crystal was always chosen.

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* *Phys. Zeitschr.* xii. p. 845 (1911).

† *Phys. Zeitschr.* xii. p. 1139 (1911).

Results are plotted with $d\mathrm{R}/\mathrm{R}$ (the change of resistance divided by the resistance in zero field) as ordinates, and with field strength, H, as abscissæ.

Tellurium, cadmium [*], *zinc, gold.*—Reference to the curves for these metals shows that the transverse effect is always greater than the longitudinal (B is for the transverse, A for the longitudinal field), but it is noticeable that the difference between the two effects approaches zero as they become smaller for different metals. It is probable that for lead or platinum, in which the effect is very small, the direction of the field would have no influence on the amount of change of resistance. In copper it would have a very slight influence.

For small fields all the curves fit the equation

$$d\mathrm{R}/\mathrm{R}=\mathrm{AH}^2,$$

but for large magnetizing forces a law of direct proportionality seems to express results better (see Grunmach's experiments [†]). The values of A for the different metals are as follows :—

	Transverse field.	*Longitudinal field.*
Tellurium	$105\cdot0 \times 10^{-12}$	$27\cdot7 \times 10^{-12}$
Bismuth [‡]	$12000\cdot0 \times 10^{-12}$	$3200\cdot0 \times 10^{-12}$(?)
Lead sulphide ...	$4\cdot86 \times 10^{-12}$	$2\cdot36 \times 10^{-12}$
Cadmium	$2\cdot88 \times 10^{-12}$	$1\cdot77 \times 10^{-12}$
Zinc	$1\cdot36 \times 10^{-12}$	$0\cdot82 \times 10^{-12}$
Gold	$0\cdot38 \times 10^{-12}$	$0\cdot32 \times 10^{-12}$

The Hall effect in tellurium is abnormally large (sixty times greater than in bismuth), so that if there is any close connexion between the Hall effect and the change of resistance in a magnetic field one would expect the curve for the latter phenomenon to exhibit abnormal properties. The relatively large values of $d\mathrm{R}/\mathrm{R}$ in tellurium, however, are small compared with $d\mathrm{R}/\mathrm{R}$ in bismuth.

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[*] See Phil. Mag. xxii. p. 900 (1911).

[†] *Ann. d. Phys.* xxii. p. 141 (1907).

[‡] From the results of P. Lenard, *Ann. d. Phys.* xxxix. p. 669 (1890)

Galenite, PbS.—Several bars of this substance were cut in different directions from a large cubical crystal and mounted as described above. Their resistances were small—about 0·2 ohm. It was found that the crystal behaved like an isotropic substance and that the curves obtained resembled those for the para- and diamagnetic metals. This was to be expected, for in all its properties lead sulphide is very similar to the metals. The addition of a sulphur atom to the molecule of lead has the effect of increasing $d\mathrm{R}/\mathrm{R}$ from 5×10^{-6} [*] to $4{\cdot}5 \times 10^{-4}$ for a field of 10,000.

Pyrites, FeS_2.—Specimens were prepared from this substance in the same way as from lead sulphide, but connexions were made by copper plating and then soldering. The drift of the galvanometer was unsteady when the bridge was in balance, as if contacts were poorly made. The fluctuations of the galvanometer made it necessary to reduce the sensibility of the apparatus, but if the magnetic field had any effect on the resistance, $d\mathrm{R}/\mathrm{R}$ for a field of 10,000 must have been smaller than 2×10^{-5}. The presence of contact resistance in lead sulphide served to increase the effect of a magnetic field. If it has the same result in pyrites probably the effect of a magnetic field could be observed if $d\mathrm{R}/\mathrm{R}$ were considerably smaller than 2×10^{-5}.

Pyrites can be magnetized, along one axis at least, so that it is an example of a ferromagnetic substance the resistance of which is unaffected by magnetization.

Molybdenite, MoS_2.—This mineral was secured through the kindness of Professor G. W. Pierce of Harvard. As molybdenite has a high specific resistance large slabs could be used for experimenting. Contacts were made by copper-plating and soldering, and here again an unsteady condition of the galvanometer resulted when balance was secured, showing that the specimen was undergoing irregular changes. These changes were often as much as 10 per cent. of the effect produced when the magnetic field acted. The curves obtained indicated a decrease of resistance, and they seemed to be affected very little by the direction of the field. It seems possible that much of the resistance lay in the contacts, so that the curve shown can hardly be taken as representing the exact behaviour of the substance. In fact, Königsberger discarded molybdenite from his experiments because of the difficulty of making electrical connexions—he found that a continual increase of pressure at the contacts produced a continual decrease of resistance.

Magnetite, $FeOFe_2O_3$.—For rods of this mineral no trouble was experienced in eliminating contact resistance. The usual method of copper-plating the ends of the rod and soldering on connexions was used, and it was found that the resistance of a given rod could be almost exactly duplicated when the leads were taken off and new ones put on in the same manner. Numerous observations were made on rods cut in various directions from a single crystal, an octahedron. A second crystal of the same form gave very similar results.

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[*] From Grunmach's results.

The curves obtained are especially interesting because they show that magnetite, though crystallizing in a regular form, has different properties along different axes. Magnetite I. is a rod cut parallel to an axis joining two opposite vertices of the crystal. Curve A is the longitudinal effect, both current and field being parallel to the length of the rod. It will be noticed that there is a slight decrease of resistance at first, but for a field of about 200 the sign changes and the substance behaves much like the ferromagnetic metals. The drop in the curve after reaching a maximum is no more than can be accounted for by inaccurate setting and the non-uniformity of the field.

Curve B is the transverse effect, the field being parallel to an edge of the crystal. Here again there is a similarity to the transverse effect in metals, especially is it like the curve for the Heusler alloy. Curve C is the transverse effect for a field rotated 90° around the rod as an axis.

Magnetite II. is a specimen cut parallel to an edge of the crystal and perpendicular to I. Curve A is the longitudinal effect and closely resembles the similar curve for Heusler alloy. The two transverse effects B and C, on the other hand, are now very unlike. They show resemblance to the longitudinal effect of I.

Magnetite III. is cut parallel to an edge of the crystal and perpendicular to I. and II. Curve A is for the longitudinal field and B and C for the transverse.

The relation between the curves can be best understood by considering only the direction of H. In I. A, II. C, and III. C, the field is in a constant direction with respect to the crystal. These curves all have points of similarity. One might expect I. A to degenerate into II. C or III. C if the magnitude of the effect were made smaller, and setting the current perpendicular to the field in II. C and III. C has evidently produced this result.

For the other curves such a relation is not easily seen. II. A and III. B are respectively longitudinal and transverse effects when H is parallel to one edge of the crystal, and

III. A and II. B are the corresponding curves when H is parallel to an edge at right angles to the first. In general one can only say that II.B and III.B become approximately equal if the current is perpendicular to the two directions it there has (see I., B & C).

Several other curves were obtained; in one, when H was perpendicular to a face of the crystal and the current flowed along an edge, a decrease of resistance as large as $13 \cdot 0 \times 10^{-4}$ per ohm was measured. Collectively the results indicate that even a regular crystal may have an exceedingly complex internal structure. The magnetic anisotropy of magnetite may be better understood if one remembers that Lord Kelvin's theory of magnetism will not be valid in the case of a ferromagnetic crystal*. A fundamental assumption of this theory is that the magnetic susceptibility, though different in different directions, is independent of the field strength. Clearly this assumption cannot be made in the case of a magnetic substance. If A, B, and C are components of magnetization and X, Y, and Z components of field strength, for a para- or diamagnetic crystal we would have the relations:

$$A = K_1 X,$$

$$B = K_2 Y,$$

$$C = K_3 Z;$$

but for a ferromagnetic substance it would be necessary to write:

$$A = X[K_1 + f_1(X^2, Y^2, Z^2)],$$

$$B = Y[K_2 + f_2(X^2, Y^2, Z^2)],$$

$$C = Z[K_3 + f_3(X^2, Y^2, Z^2)].$$

For a regular non-magnetic crystal the susceptibility is the same along all the axes, so that $K_1 = K_2 = K_3$, and the equations are the same as for an isotropic substance. For a regular magnetic crystal, however, we have the terms $f(X^2, Y^2, Z^2)$ entering, and these functions cannot be taken as the same along all the axes even if the crystal belongs to the regular system.

In the case of magnetite Weiss † has shown experimentally that a regular ferromagnetic crystal may have different properties along different axes, and his work, together with that of V. Quittner ‡, indicates that magnetite is even more complex in structure than pyrrhotine, which does not belong to the regular system. Weiss and Quittner used relatively small fields, but their results seem to indicate magnetic isotropy after saturation is reached. It is of interest to note that this anisotropic character of magnetite as shown by the change of resistance in a magnetic field persists long after the saturation point is passed.

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* See Voigt, *Gött. Nachr.* p. 331 (1900).

† *Journ. d. Phys.* v. p. 435 (1896).

‡ *Ann. d. Phys.* p. 289 (1909).

In general, all the results obtained may be summarized as follows:—

1. For para- and diamagnetic metals a transverse field produces a greater increase of resistance than a longitudinal field, and for small magnetizing forces the increase is proportional to the square of the field strength.

2. Crystals of lead sulphide in a magnetic field behave like an isotropic para- or diamagnetic metal.

3. The resistance of iron pyrites is unaltered by a magnetic field—at least, if there is a change, it is smaller than 2×10^{-5} per ohm for a field of 10,000.

4. Whatever the direction of the magnetizing force, the resistance of molybdenite decreases, and it decreases in much the same way as does the resistance of Heusler alloy in a longitudinal field.

5. The behaviour of magnetite in a magnetic field indicates that this mineral has a very complex internal structure; it has different properties along different axes even when subjected to magnetizing forces much greater than are necessary to produce saturation. For fields greater than four or five thousand, after the magnetization has reached a maximum, $d\text{R}/\text{R}$ and H are always connected in a linear relation. Indeed, this seems to be the case for everything examined, provided a large enough field can be secured.

As far as the crystalline structure of metals is concerned, one could say that for a non-magnetic substance crystallizing in regular form, the internal crystalline structure would have no effect on the change of resistance in a magnetic field. For ferromagnetic metals, however, this crystalline character might play a rather important role, since the orientation of the minute crystals might influence the general change of resistance caused by magnetization.

It is again a pleasure to thank Professor E. P. Adams for his advice and for the helpful interest he has taken in the work.

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LXXXVII. *On Uniform Rotation, the Principle of Relativity, and the Michelson-Morley Experiment.*

By J. W. Nicholson, *M.A., D.Sc., Professor of Mathematics in the University of London* [*].

SOME discussion has taken place recently with regard to the bearing of the principle of relativity on problems of uniform rotation. Usually the validity of an application of this principle has been assumed. The principle may be regarded from two points of view. In the first place, it may be postulated, as by Einstein and others, for the case of uniform translation, in the form of a general law underlying the description of electromagnetic phenomena, quite apart from its actual analytical origin. Secondly, it may be derived, as originally by Larmor, from the result of an analytical transformation applied to the variables in a set of equations occurring in electromagnetic theory. When approached from this standpoint, it is endowed with a mode of proof which is otherwise lacking, although invested with certain difficulties of detail. For the case of a system in uniform translation, a complete correlation between the sequence of events in this system referred to axes moving with it, and the sequence in a corresponding fixed system, can be established. This correlation is contained to any order of approximation in the equations developed by Larmor, who, however, in his treatise, discussed the more detailed theory of the matter only to the second approximation needed for the description of the null result of such experiments as that of Michelson and Morley, or the efforts of Lord Rayleigh and Brace to detect a double refraction in bodies on account of the earth's motion. Subsequent writers, following Lorentz and Einstein, have developed the detailed theory to any relative magnitude of the velocity of translation to that of light.

The principle of relativity, in the case of uniform velocity of translation, was thus suggested at first by analysis, although, in the words of Lorentz, the scaffolding by which it was originally built up has been removed, and the principle postulated *a priori* as giving a consistent account of phenomena. But when consideration is directed from motion of translation to motion of uniform rotation, it appears that a corresponding analytical basis has not been given to the principle, and the two points of view begin to diverge. It is not a matter for surprise that any attempt to extend the scope of the principle into this domain leads to immediate difficulties. Ehrenfest[*] has propounded the paradox that if a disk is spinning uniformly, any circle of a concentric system must contract in a definite ratio defined by the velocity of one of its points, for each element of its arc is moving along the tangent with a uniform velocity. Yet at the same time, the radius of the circle, which has no motion along its length, should not alter. An ingenious mode of reconciling these statements has been devised by Stead and Donaldson[†], who suggest that the rotation causes the disk to buckle inwards, taking the form of an epicycloidal surface of revolution when the rotation is small. They also regard it as probable that a solid cylinder would be more likely to remain in a state of strain. It appears that the requirements of the principle of relativity can be satisfied in this way, although it might perhaps be preferable, in place of the somewhat unsatisfactory hypothesis of straining, to suppose that the cylinder became distorted so that normal circular sections became parallel surfaces, epicycloidal for small rotation about the axis.

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[*] Communicated by the Author.

There are many other difficulties connected with uniform rotation. For example, if a disk of sufficient radius were set into rotation, the particles at a sufficient distance from the axis would acquire a velocity greater than that of light, as Mr. A. A. Robb suggested to me in the course of a discussion. Quite apart from the principle of relativity, therefore, if it is possible to set a disk of sufficient size into rotation, the only way of representing the phenomena which must occur, by the medium of ordinary geometry, appears to be by a supposition of a buckling effect, in default of an indefinite contraction of the radius.

The essential distinction between uniform rotation and uniform translation is, from one point of view, the presence of a normal acceleration in the former, and this must render the principle of relativity, at any rate in its ordinary form, inconsistent with the electromagnetic equations. But this normal acceleration is proportional to the square of the angular velocity, and therefore cannot introduce more than a second order effect into the general nature of the scheme of vectorial relations appropriate to translational motion, for distances from the axis whose product with the angular velocity is small in comparison with the velocity of light. The principle of relativity must therefore be valid as a first order principle, as will be shown analytically below. The exact extent of the divergence between the cases of rotation and translation is of course important in the theory of the Michelson-Morley experiment. The statement is frequently found that such an experiment would give a null result if the experimental accuracy were more refined. This is incorrect if the circuital relations are a valid foundation for electromagnetic theory, for it will be shown that they must apparently lead to an effect, although of a higher order than any experiment yet devised can detect. The effect may be of the second order in the velocity ratio, but actually of higher order than this on account of the large radius of the earth. The assumption that the earth's motion may be treated as translation for a point on its surface has always been tacitly made, with of course sufficient justification from first principles when terms beyond the square of the velocity ratio are neglected. The explicit statement of the ground of the assumption, or of its exact order of validity, does not appear to have been made, nevertheless, although there is no necessity for invoking the subsequent analysis of this paper in order to obtain it.

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[*] *Phys. Zeit.* November 1909.

[†] Phil. Mag. July 1910; March 1911.

Swann * has drawn attention to the normal acceleration as a factor destroying the principle of relativity for rotation, but his analysis is vitiated by the use of an incorrect form of the solenoidal relations of the vectors, which leads to the conclusion that even to the first order, the correspondence between the fixed and moving systems will not, in general, be found. This, as we have seen, cannot be correct. The analysis in other respects proceeds on the natural lines initiated by Larmor and Lorentz in their treatment of uniform translation in one direction.

In this paper, a formal examination is made of the limits within which a correlation can be obtained on the ordinary analytical lines. It will appear that a second order correspondence cannot be found, so that the geometry of uniform rotation cannot be expressed in a simple general way. This is not an unexpected result, since the case of uniformly accelerated motion in one direction, which is probably of simpler character, has not been so expressed.

Let a set of cylindrical coordinates (r, θ, z) be chosen, where z is the axis of rotation of a system. If $(f\ g\ h)$, $(a\ b\ c)$ are the components of polarization and magnetic induction along r, θ, and z respectively increasing, their time rates with respect to axes in which the initial line of

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* Phil. Mag. March 1911.

measurement of θ does not rotate, are given by

$$\left.\begin{aligned}4\pi r\frac{\partial f}{\partial t}&=\frac{\partial c}{\partial\theta}-r\frac{\partial b}{\partial z}\\4\pi\frac{\partial g}{\partial t}&=\frac{\partial a}{\partial z}-\frac{\partial c}{\partial r}\\4\pi r\frac{\partial h}{\partial t}&=\frac{\partial}{\partial r}(br)-\frac{\partial a}{\partial\theta}\end{aligned}\right\}, \quad . \; . \; . \; . \; . \quad (1)$$

with a similar set of equations obtained by writing (f, g, h) for (a, b, c) and $-(4\pi C^2)^{-1}(a, b, c)$ for $4\pi(f, g, h)$, where C is the velocity of light.

Consider now a new set of axes rotating round z with angular velocity ω. If accented coordinates are those relative to these axes, we may write

$$r'=r, \quad z'=z, \quad t'=t, \quad \theta'=\theta-\omega t,$$
$$\partial/\partial r=\partial/\partial r', \quad \partial/\partial z=\partial/\partial z', \quad \partial/\partial\theta=\partial/\partial\theta',$$
$$\partial/\partial t=\partial/\partial t'-\omega\partial/\partial\theta'.$$

The solenoidal conditions are

$$\frac{\partial}{\partial r}(fr)+\frac{\partial g}{\partial\theta}+r\frac{\partial h}{\partial z}=\frac{\partial}{\partial r}(ar)+\frac{\partial b}{\partial\theta}+r\frac{\partial c}{\partial z}=0, \; . \quad (2)$$

where the variable coordinates may be accented.

We derive three equations in the new variables, the first being

$$4\pi r\frac{\partial f}{\partial t'}=\frac{\partial}{\partial\theta'}(c+4\pi r\omega f)-r'\frac{\partial b}{\partial z'}.$$

If

$$\left.\begin{aligned}(a', b', c')&=(a-4\pi r\omega h,\ b,\ c+4\pi r\omega f)\\(f', g', h')&=\left(f+\frac{\omega rc}{4\pi c^2},\ g,\ h-\frac{\omega ra}{4\pi c^2}\right)\end{aligned}\right\}; \; . \; . \; . \quad (3)$$

then the three equations are similar to (1), the first being

$$4\pi r'\frac{\partial f}{\partial t'}=\frac{\partial c'}{\partial\theta'}-r'\frac{\partial b'}{\partial z'}. \; . \; . \; . \; . \; . \; . \quad (4)$$

The variables without accent may be eliminated after the usual manner. We find, if

$$\epsilon^{-1}=1-\omega^2r^2/C^2, \quad . \; . \; . \; . \; . \; . \quad (5)$$

$$\left.\begin{aligned}\epsilon^{-1}(a, b, c)&=(a'+4\pi\omega r'h',\ \epsilon^{-1}b',\ c'-4\pi\omega r'f')\\\epsilon^{-1}(f, g, h)&=(f'-\omega r'c'/4\pi C^2,\ \epsilon^{-1}g',\ h'+\omega r'a'/4\pi C^2)\end{aligned}\right\} \quad (6)$$

where ϵ is a function of r.

Substituting in the set of equations typified by (4),

$$\left.\begin{aligned} 4\pi\epsilon r'\frac{\partial f'}{\partial t'} &= \left(\frac{\partial}{\partial\theta'}+\frac{\epsilon\omega r'^2}{C^2}\frac{\partial}{\partial t'}\right)c'-\frac{\partial}{\partial z'}(b'r') \\ 4\pi\frac{\partial g'}{\partial t'} &= \frac{\partial a'}{\partial z'}-\frac{\partial c'}{\partial r'} \\ 4\pi\epsilon r'\frac{\partial h'}{\partial t'} &= \frac{\partial}{\partial r'}(b'r')-\left(\frac{\partial}{\partial\theta'}+\frac{\epsilon\omega r'^2}{C^2}\frac{\partial}{\partial t'}\right)a' \end{aligned}\right\}. \qquad (7)$$

A variation in the usual procedure for Cartesian coordinates must now be introduced, ϵ being variable. Write $\rho^2=\epsilon r'^2$, so that

$$\rho^2=r'^2/(1-\omega^2r'^2/C^2), \quad . \quad . \quad . \quad . \quad (8)$$

and conversely,

$$r'^2=\rho^2/(1+\omega^2\rho^2/C^2), \quad \epsilon=1+\omega^2\rho^2/C^2, \quad . \quad . \quad (9)$$

so that

$$d\rho/dr'=\rho^3/r'^3, \quad \rho d\rho/r'dr'=\epsilon^2. \quad . \quad . \quad . \quad (10)$$

The length ρ is a radius vector in a certain distorted space which may be derived from the original space by a non-uniform extension perpendicular to the axis, around which it is symmetrical. If dA is a polar element of area in this space between two radii of length ρ enclosing an angle $d\theta'$, then $dA=\frac{1}{2}\rho^2d\theta'$. Let the time variable be changed from t' to t'', where

$$t''=t'-2\omega A/C^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Then $\partial/\partial t'$ becomes $\partial/\partial t''$, and $\partial/\partial\theta'+\epsilon\omega C^{-2}r'^2\partial/\partial t'$ becomes $\partial/\partial\theta'$. Accordingly,

$$\left.\begin{aligned} 4\pi\epsilon r'\frac{\partial f'}{\partial t''} &= \frac{\partial c'}{\partial\theta'}-\frac{\partial}{\partial z'}(b'r') \\ 4\pi\frac{\partial g'}{\partial t''} &= \frac{\partial a'}{\partial z'}-\frac{\partial c'}{\partial r'} \\ 4\pi\epsilon r'\frac{\partial h'}{\partial t''} &= \frac{\partial}{\partial r'}(b'r')-\frac{\partial a'}{\partial\theta'} \end{aligned}\right\}, \quad . \quad . \quad . \quad (12)$$

with similar equations for the time rate of the magnetic vector.

These equations are of the same form as those from which we started, except for the factors ϵ on the left. Since these differ from unity by amounts of the second order (for proper values of r'), the correspondence between the fixed and moving systems follows in the usual way to the first order.

The difference between r and ρ is only of the second order, but the vectors and the time differ from the stationary values by first order terms, as in the theory of translation.

But we cannot proceed in the ordinary way to a more complete correspondence, mainly on account of the term $\partial/\partial r'(r'b')$ in the last equation. It is evident that a new time variable t_1 for which dt_1 is a perfect differential cannot be employed without introducing time differentiations on the right, and it may be shown that, in particular, the transformation required by either the principle of relativity or the buckling theory of the rotating body cannot reduce the equations to the old type, even with any readjustment of the vectors concerned.

The principle of relativity thus cannot be derived analytically for the case of rotation, except as a first order principle, and as we have seen, its extension beyond the problems contemplated by Einstein is not warranted. We must therefore, since the motion of the earth is not translation, expect second order velocity effects due to the motion of the earth in experiments like those of Michelson and Morley. But these effects are, by virtue of another factor, incapable of detection by present experimental means. Let a be the radius of the earth, and consider an experiment performed at its surface. The value of ϵ^{-1} is

$$\epsilon^{-1}=1-\omega^2(a+\xi)^2/C^2,$$

where ξ is the height of a point above the surface. If $\delta^{-1}=1-\omega^2 a^2/C^2$, make the transformation

$$\left.\begin{array}{r} dt''=\delta^{\frac{1}{2}}\,dt_1,\ (a_1,\delta^{\frac{1}{2}}b_1,c_1)=(a',b',c'), \\ (f_1,\delta^{\frac{1}{2}}g_1,h_1)=(f',g',h'),\ (r_1,z_1)=(r',z'),\ d\theta_1=\delta^{-\frac{1}{2}}d\theta' \end{array}\right\}. \quad (13)$$

Then the equations (12) are unaltered in type except for a substitution of ϵ/δ for ϵ. But $\epsilon/\delta=1+2\omega^2 a\xi/C^2$, and the equation of this quantity to zero can only affect the result of any experiment, as prophesied by the equations, to a relative order $\omega^2 a\xi/C^2$ or $v^2\xi/aC^2$, where ξ is the greatest length concerned in the apparatus, and v is the surface velocity.

The value of ξ in the Michelson-Morley experiment was about 20 metres, so that ξ/a is of order 10^{-6}. But v^2/C^2 is of order 10^{-14} approximately, so that the final effect is actually of the third order in the velocity ratio, by virtue of the other factor. Morley and Miller * found it possible to conclude that if there is any effect of this nature it is less than one

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* Phil. Mag. [6] ix. p. 680 (1905).

hundredth of the order v^2/C^2. The analysis provides for this result. But it is not correct to suppose that the effect is non-existent, in the absence of the principle of relativity. The effect of the earth's orbital motion is of course smaller.

A brief treatment of the same problem by the Cartesian method is of analytical interest. If z is the axis of rotation, and (λ, μ, ν) is any vector referred to the axes which rotate round z with uniform angular velocity ω, then its rate of change with respect to fixed axes coinciding instantaneously with the moving axes, has components

$$\partial/\partial t'\ (\lambda, \mu, \nu) - \omega(\mu, -\lambda, 0),$$

where $\partial/\partial t'$ denotes a differentiation referred to moving axes, as against $\partial/\partial t$ referred to axes fixed in the æther. These must be identical with $\delta/\partial t\ (\lambda, \mu, \nu)$ or

$$(\partial/\partial t - \omega y \partial/\partial x + \omega x\, \partial/\partial y)(\lambda, \mu, \nu).$$

Thus

$$(\partial/\partial t)(f, g, h) = (\partial/\partial t' + \omega y\, \partial/\partial x - \omega x\, \partial/\partial y)(f, g, h) - \omega(g, -f, 0). \quad . \quad (14)$$

But, with fixed axes,

$$4\pi\, \partial/\partial t\ (f, g, h) = \text{curl}\ (a, b, c), \quad . \quad . \quad . \quad (15)$$

so that, with respect to axes moving with a terrestrial observer and with his instruments, we obtain on reduction

$$4\pi\, \partial/\partial t'\ (f, g, h) = \text{curl}\ (a, b, c) + 4\pi\omega\, \text{curl}\,(-hx,\ -hy,\ fx + gy),$$

or

$$4\pi\, \partial/\partial t'\ (f, g, h) = \text{curl}\ (a', b', c'), \quad . \quad . \quad (16)$$

where

$$a' = a - 4\pi\omega x h, \quad b' = b - 4\pi\omega y h,$$
$$c' = c + 4\pi\omega\ (fx + gy). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

After the same manner

$$\partial/\partial t'\ (a, b, c)) = -4\pi C^2\ \text{curl}\ (f', g', h'), \quad . \quad . \quad (18)$$

where

$$f' = f + \omega x c/4\pi C^2, \quad g' = g + \omega y c/4\pi C^2,$$
$$h' = h - \omega\ (ax + by)/4\pi C^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

A solution of these equations yields, if $\epsilon^{-1}=1-\omega^2(x^2+y^2)/\mathrm{C}^2$,

$$\left.\begin{aligned}
\epsilon^{-1}a&=a'(1-\omega^2y^2/\mathrm{C}^2)+4\pi\omega xh'+\omega^2xyb'/\mathrm{C}^2\\
\epsilon^{-1}b&=b'(1-\omega^2x^2/\mathrm{C}^2)+4\pi\omega yh'+\omega^2xya'/\mathrm{C}^2\\
\epsilon^{-1}c&=c'-4\pi\omega(xf'+yg')\\
\epsilon^{-1}f&=f'(1-\omega^2y^2/\mathrm{C}^2)-\omega xc'/4\pi\mathrm{C}^2+\omega^2xyg'/\mathrm{C}^2\\
\epsilon^{-1}g&=g'(1-\omega^2x^2/\mathrm{C}^2)-\omega yc'/4\pi\mathrm{C}^2+\omega^2xyf'/\mathrm{C}^2\\
\epsilon^{-1}h&=h'+\omega(a'x+b'y)/4\pi\mathrm{C}^2.
\end{aligned}\right\}\quad . \quad . \qquad (20)$$

On substitution in (16) the circuital relations take the form, quoting only the first,

$$4\pi\frac{\partial}{\partial t'}\left\{\epsilon j'(1-\omega^2y^2/\mathrm{C}^2)+\frac{\omega^2\epsilon\,xy}{\mathrm{C}^2}y'\right\}=\left(\frac{\partial}{\partial y}+\frac{\omega\epsilon x}{\mathrm{C}^2}\right)c'-\frac{\partial b'}{\partial z'}.$$

Take now a new time variable t'' such that

$$dt''=dt'-\omega\epsilon(xdy-ydx)/\mathrm{C}^2, \quad . \quad . \quad . \quad . \qquad (21)$$

which may be recognized at once as identical with the time chosen in the other method, for $xdy-ydx=r^2d\theta$. Then if

$$\epsilon_1^{-1}=1-\omega^2x^2/\mathrm{C}^2,\ \epsilon_2^{-1}=1-\omega^2y^2/\mathrm{C}^2, \quad . \quad . \qquad (22)$$

we obtain

$$4\pi\frac{\partial}{\partial t''}\left(\frac{\epsilon}{\epsilon_2}f'+\frac{\omega^2\epsilon\,xyg'}{\mathrm{C}^2},\ \frac{\epsilon}{\epsilon_1}g'+\frac{\omega^2xy^2\epsilon f'}{\mathrm{C}^2},\ \epsilon h'\right)=\operatorname{curl}\,(a',\ b',\ c'),$$
$$. \quad . \quad . \quad . \quad . \qquad (23)$$

with similar magnetic equations. Since the functions ϵ only differ from unity by amounts of the second order, the equations have, to the first order only, reverted to the original type. The remainder of the argument then follows along the previous lines.

LXXXVIII. *The Indices of Doubly-refracting Crystals, Determined by Displacement Interferometry.* *By* Carl Barus, *Ph.D., LL.D.*[*]

1. *INTRODUCTION. METHOD.*—In the following paper I shall make a further application of the displacement interferometer, in endeavouring to investigate a method for the determination of the two refractions of a crystalline plate, with a degree of accuracy approaching the spectrometer and eventually to exceed it. The work is to be extended to all directions of the ordinary and extraordinary ray within the crystal. Inasmuch as the centre of ellipses

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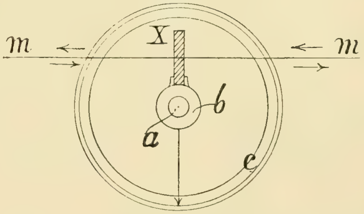
[*] Communicated by the Author. Abridged from a Report to the Carnegie Institution of Washington, D.C.

is never lost, but may always be brought back again to the fiducial and coincident sodium lines by moving the micrometer, however remote the centre may be, a crystal (or indeed a column of any thickness) may be placed in one of the component beams, and the micrometer equivalent of the difference resulting from presence and absence of the crystal ascertained. This makes the method quite sensitive; for the two micrometer readings for the presence of air and crystal, respectively, may differ by many centimetres, if desirable, and each reading may be to ·00005 centimetre.

The method, however, requires an accurately plane parallel plate, however thick. If the faces are at even a slight angle, the beam passing through them will be deflected by the introduction of the crystal and will not be returned in its own path. This requires a readjustment, and therefore a correction for the displacement of the mirror difficult to estimate. It is to be accentuated, however, that the method for normal incidence admits of a plate of any thickness, *i. e.*, of a long column of glass with plane parallel end faces, so that this method of measuring the index of refraction must ultimately exceed in sensitiveness the method of the spectrometer, while even the importance of the readjustment in question becomes of less consequence. It will thus be available for answering refined questions relative to this index even in glass, under conditions where the spectrometer fails of application. It is in this direction that the results are to be prosecuted as soon as the preliminaries discussed in the present paper have been clarified.

It is also probable, that if the deviation of the ray *mm* due to non-parallel faces in the crystal is corrected not at the micrometer mirror M, but at the other opaque mirror N beyond the grating, the discrepancy in question will vanish. For in this case, on restoring the interferences by rotating N, the air path of *both* component beams *mm* and *nn* is equally incremented.

Fig. 1.



The plate crystal X may be mounted on a horizontal axle *ab* (fig. 1) normal to the interfering beam *mm* in question.

The angle of incidence of the beam is changed by rotating the plate in definite steps and the amount of rotation read off on the attached fixed graduated circle *c*, with its plane parallel to the beam and its axis normal to it. Angles of 0°, 10°, 20°, 30°, 40°, and even 50°, were usually available on either side of the normal position. The crystal, mounted in a cork plate, was at first conveniently held by a spring clip; but later*, more elaborate means for mounting the plate parallel to the axis of rotation were adopted. The normal position is found with certainty by slightly rotating the crystal around the horizontal axis in either direction, until the interference rings in the field of view change their direction of motion. This, for the ordinary ray, determines the minimum thickness e. The same operation is then performed around the vertical axis, both adjustments being usually easy and the result satisfactory.

With the angle i given, the corresponding angle of refraction, r, i. e., the angle of the ray with the optic axis of the crystal, may be computed when the index of refraction for the given case is known. Hence the refractions in different directions, r, both for the ordinary and extraordinary ray, follow, as far as about $r=30°$ from the optic axis, in the above apparatus. Plates are not usually large enough for a larger internal angle on the one hand, while the errors of measurement multiply on the other; but by selecting a plate cut parallel to the axis, the final 30° of the quadrant may be found. To obtain the intermediate 30° a plate cut obliquely to the axis or else a plate of large area would be necessary.

When the plate is cut parallel to the axis and the difference of the refractive indices (as in quartz) not too large, the two interferometer ellipses, corresponding to the ordinary and extraordinary rays, are in the field at once, making an exceedingly beautiful design. Their distance apart may then be found micrometrically in terms of the refraction of the ordinary ray, giving an acceptable datum even in case of an imperfect, *i. e.,* slightly wedge-shaped plate. In other words, the ordinary and extraordinary rays encounter the same conditions, and their difference of path remains practically unimpaired.

To distinguish between the two families of intersecting ellipses, it is necessary to polarize the incident beam in the vertical and horizontal plane, respectively, seeing that the crystal is revolvable about the horizontal or vertical axis. When the plate is true and the mounting trustworthy there need never be difficulties due to elliptical polarization, for the vertical and horizontal vibrations pass unchanged. If, however, rotary polarization occurs, the case of the oblique path is more complicated, but it does not interfere with the measurement.

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* It will be shown below that the eccentric mounting of the crystal, as in fig. 1, is not, as a rule, advisable.

The present method inherently presupposes a knowledge of the dispersion of the crystal. Whenever this term is of the nature of a correction, the coefficient in the simplified Cauchy equation of two terms may, at the outset, be inserted. For accurate work Cauchy's equation as far as the fourth power of wave-length must be used. It will be shown moreover, that the method is self-contained, by affording means for determining the coefficients of the equation in question. Initially no more than a measurement of the refraction of the extraordinary ray in terms of the ordinary ray will be attempted. The dispersion constant found for these rays from data for two Fraunhofer lines may then be used for all wave-lengths lying between.

2. *Equations.*—If e', I, R, μ', denote the thickness, the angles of incidence and refraction, and the index of refraction of the grating, and e, i, r, μ, the corresponding quantities for the plane parallel plate inserted in one of the component beams of the interferometer; if, furthermore, b' and b denote the corresponding coefficients in the simplified dispersion equation of Cauchy $\mu=a+b/\lambda^2$, so that

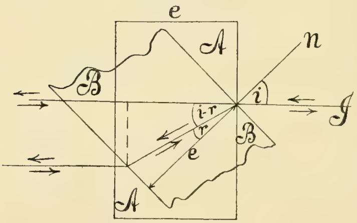
$$-\lambda d\mu/d\lambda=2b/\lambda^2,$$

the coordinates of the micrometer in the absence of the plate will be, if μ_a is the absolute index of refraction of air,

$$\mathrm{N}'=e'\mu'\left(\cos \mathrm{R}+\frac{2b'}{\lambda^2\mu'\cos \mathrm{R}}\right)+e\mu_a, \quad . \quad . \quad . \quad (1)$$

where $e\mu_a$ is the air-path coextensive with the thickness of the plate in its normal position AA (fig. 2), I being the incident beam of light. If the plate is inserted at an angle

Fig. 2.



of incidence i in the position given by BB, and the centre of ellipses is then returned to the same fiducial line D of the spectrum, by moving the opaque mirror on the micrometer over a distance ΔN, nothing has been changed at the grating, and the first term of the right-hand member of equation (1) remains unchanged. It therefore vanishes so far as ΔN is concerned. Hence we may write

$$\mu_a(e+\Delta N)=\frac{e}{\cos r}\left(\mu+\frac{2b}{\lambda^2}\right)+e\mu_a\left(1-\frac{\cos(i-r)}{\cos r}\right), \quad (2)$$

as fig. 2 shows. For not only has the path e been increased, by the introduction of the oblique plate, but the air-path is also longer. On removing $e\mu_a$

$$\mu=\mu_a\left(\frac{\Delta N\cos r}{e}+\cos(i-r)\right)-\frac{2b}{\lambda^2}. \quad . \quad . \quad (3)$$

In this equation the quantities μ, r, refer to the same fiducial spectrum line of wave-length λ, to which the centre of ellipses is always to be restored by moving the micrometer. Whenever the incidence at the plate is normal, $i=r=0$,

$$\mu=\mu_a\left(\frac{\Delta N}{e}+1\right)-\frac{2b}{\lambda^2}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

an equation more generally useful and particularly so in case of long columns.

If the dispersion of air cannot be disregarded, μ_a must be replaced by $\mu_a(1+2b''/\lambda^2\mu_a)$, μ_a and b'' referring to a plenum of air. Equation (3) is then modified by replacing the last term by

$$-2(b-b'')/\lambda^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Since $\mu\cos r=\sqrt{\mu^2-\sin^2 i}$, equation (3) is essentially of the fourth degree and can be solved only by approximation. This, however, is rapid; for $\mu-1$, nearly, is computed in terms of μ, which is always relatively more accurate than $\mu-1$. In Table I. the values of the micrometer displacements ΔN are given under varying conditions of illumination, but all under normal incidence, $i=r=0$. It is probable that the differences of value of ΔN found are owing simply to the distortion of the ellipses in the different cases.

TABLE I.

Quartz plate normal to axis. $e = \cdot 5996$ cm. $i = r = 0°$.
Sunlight.

Remarks.	ΔN.
Short collimator. Ellipses centred	·34025
No collimator. Sunlight and slit. Ellipses not centred	·34000
Do. Ellipses centred, but distorted	·34020
Do. Ellipses centred	·34040
Weak objective as collimator. Ellipses less distorted	·34015
Do. with large telescope	·34050
Short collimator. Sharp ellipses	·34040
Concave lens added to collimator	·34060

The beam, in case of sunlight, is sheet-like, with its long dimension vertical. Much of it is lost over the edge of mirrors, on successive reflexion. The arc lamp and a collimator objective which places the focus (relatively to the vertical plane) on the opaque mirrors M and N furnish a rapier-like beam. This may easily be made to penetrate tubes and columns as a whole. It is thus far preferable and the results better. The sodium line is invariably present, as a line of reference for measurement.

3. *Dispersion Constants.*—In the equation in the normal form (4) for two wave-lengths λ and λ', b may be eliminated or determined; for if $y = \sin i = 0$ (normal incidence, detected with certainty by the inversion in the motion of the rings as described above), $x = \Delta N/e$, and $\mu = A + b/\lambda^2$ is assumed for a sufficiently narrow range of the spectrum near the D line,

$$A = \mu_a(1 + x\lambda^2 - x_1\lambda_1^2)/(\lambda^2 - \lambda_1^2), \quad . \quad . \quad . \quad (6)$$

$$3b = \mu_a\lambda^2(x - x_1)/(1 - (\lambda/\lambda_1)^2). \quad . \quad . \quad . \quad . \quad (7)$$

If the value of x is restored, since for the two wave-lengths

$$\Delta N = N' - N \quad \text{and} \quad \Delta N_1 = N_1' - N_1,$$

where N′ refers to glass and N to air,

$$e(x_1 - x) = N_1' - N_1 - (N' - N) = N_1' - N' - (N_1 - N),$$

or briefly
$$e(x_1 - x) = \delta N' - \delta N,$$

whence
$$b = \frac{\mu_a\lambda^2}{3e} \frac{\delta N' - \delta N}{1 - (\lambda/\lambda_1)^2}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here δN′ and δN are the differences of micrometer readings for the two spectrum lines λ and λ′, for glass in place and for glass removed, respectively. ΔN_1 and ΔN need not therefore be known, *i. e.*, the glass plate need not be scrupulously plane parallel, as it is merely necessary to get the glass difference and the air difference for two successive lines, however far apart the air and glass positions may be for either line. Equation (8) also follows at once from (3) by inserting the equivalent of μ for the two spectrum lines.

Granting the approximate form of Cauchy's equation, the error of b thus obtained should be well within 1 per cent. Its influence on μ should not exceed one unit in the fourth place. Unfortunately, however, the equation in question is not warranted to this extent when the lines of the spectrum are as far apart as D and E, for instance. Tho question relative to b will be resumed in § 5. Meanwhile I may observe that the dispersion equation with three constants would need three spectrum lines for the determination of the two essential constants. This is a cumbersome procedure, but from the nature of the problem is nevertheless probably the only resort; particularly in the case where a long column of glass, crystal, or liquid is to be investigated, for exceptionally accurate indices of refraction.

In conclusion it is worth while to determine the value of μ_ϵ in terms of μ_0 found from the normal position, when the difference of these indices (as in quartz) is not large. In fact, since $d(\Delta \mathrm{N})=e\,dx$,

$$\frac{d\mu}{d(\Delta \mathrm{N})}=\frac{\mu\cos^2 r}{e\mu\cos r/\mu_a-\Delta \mathrm{N}\sin^2 r+e\sin r\sin(i-r)}. \qquad (9)$$

If $i=r=0$, this reduces to

$$\frac{d\mu}{d(\Delta \mathrm{N})}=\frac{\mu_a}{e}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

If in equation (9) the value of μ_0 is introduced, the corresponding value of μ_ϵ may be computed from the $\Delta \mathrm{N}$ and $\Delta \mathrm{N}'$, which put the two ellipses, respectively, on the fiducial sodium line. The result gives a fair value for μ_ϵ, even when μ_0 varies with the incidence i due to errors of adjustment, seeing that μ_0 must be constant and is found from the normal position.

4. *Oblique Incidence.*—The incident light was polarized in the vertical plane before reaching the slit, the D line being as usual fiducial. When viewed through an analyser, the light reaching the telescope in case of the more oblique positions of the plate on its horizontal axis was elliptically polarized in one of the superimposed spectra, the latter showing the usual channeled structure with more dark bands

as the effective thickness increased. With obliquity decreasing through zero, moreover, the black bands between crossed nicols moved in opposite directions when the normal position was passed. For the polarizer at 45° both families of ellipses were in the field at once. Either one or the other set could be excluded by rotating the analyser. In the absence of this, the field showed the ordinary or the extraordinary set of ellipses separately, on rotating the polarizer 90°. In the further absence of the polarizer, one frequently observes dislocated rings, the dislocation being in multiple along equidistant vertical planes. In such loci the ordinary and extraordinary rings, therefore, successively passed into each other. In general a figure which is blurred without the polarizer is resolved into two clean figures by the aid of it, one being definitely displaced with reference to the other.

A large number of experiments was made, not only with crystals cut normally or parallel to the axis, but with plates of crown and of flint glass. In most cases, however, the plates were inadequately plane parallel, and the absolute value of the index of refraction was distorted in view of the insertion of the slightly wedge-shaped crystal. Table II. is a sufficient example of these results, as a whole. The data were obtained with a plate of quartz, here adequately true, the axis of rotation being vertical and made parallel to the face of the crystal by the device of a perforated axle, which need not be described here. Unfortunately the face of the crystal was somewhat small, so that large angles of incidence were inadmissible. In such a case the axis of rotation should pass symmetrically between the faces, which was not quite feasible in the case of the given apparatus.

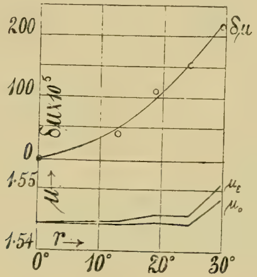
TABLE II.

Plane parallel plate of quartz ("rouge"), lozenge-shaped, cut normal to the axis. $e = \cdot 5996$ cm.; $\mu_0 = 1\cdot 54423$; $b = \cdot 421 \times 10^{-10}$. Vertical axis of rotation.

i.	r.	$10^5 \times \Delta N_0$.	Observed μ_o.	$10^5 \times \Delta N_\epsilon$.	Observed μ_ϵ.	$10^5 \times \delta\mu$.
0°	0°	34059	1·54423	34059	1·54423	0
20	12·80	35414	1·54426	35439	1·54466	40
30	18·88	37211	1·54465	37280	1·54575	110
40	24·60	39825	1·54422	39925	1·54575	153
50	29·73	43781	1·54827	43944	1·55063	236

The results of this table are reproduced in fig. 3, the lower curves showing the individual indices of refraction, and the upper curve giving their difference. When $i=50°$ or $r=30°$ (nearly), the rays pass too near the edge, so that measurement is uncertain, because some of them are excluded. For large r, moreover, the interpretation is complicated by the occurrence of rotary polarization along the axis. The data for $\delta\mu$ fluctuate to within a few units of the fourth place, which is to be expected for the given thickness of plate used.

Fig. 3.



5. *Results for Different Spectrum Lines.*—In § 3 the method for computing the approximate dispersion constant b was indicated. There is, however, a difficulty inherent in this method inasmuch as for the case where μ is to be found for four or more places of decimals, the abbreviated Cauchy equation is insufficient.

Leaving this for the present, it is interesting to compare the results obtainable by the interferometer with the standard data of Mascart and de Lépinay and others [*]. For this purpose the quartz of Table II. was mounted at normal incidence and the micrometer readings for the C, D, E, b, F lines of the spectrum taken in succession, both for the presence and absence (air) of the quartz plate. The differences of corresponding values (quartz and air) of δN for the same line were then reduced to the value of ΔN for the D line in Table II., so that the ΔN for each spectrum line was obtained in succession for the computation of μ. In other words, the values of δN are shifted so that for the sodium line $\delta N_D=0$.

The results show that the value of μ thus computed differs from the value of Mascart, μ_M, by fourteen units in the fourth place in case of the extreme C and F lines. The reason of this is the approximate value of b taken. To find what the value of b should have been in each case put

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[*] See Landolt and Börnstein's Tables.

$$\mu_M = M \text{ and } \mu_a(\Delta N/e+1) = S;$$

then

$$(M-S)\lambda^2 = -2b. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The values of b so obtained show a very appreciable variation in the march of b from the C to the F line, viz.,

Line	C	D	E	b	F
Mean $b\times 10^{-10}$.	·446	·421	·403	·405	·398

If the mean value of b is computed from Mascart's data *, between the C and D and the D and E lines, and compared with the computed mean of the table, the results are

	C to D.	D to E.
Mascart...........	$b\times 10^{-10}=$·421	·407
Interferometer ...	$b\times 10^{-10}=$·433	·412

a difference of about 3 and 1 per cent., respectively. But the C line in the grating interferometer is difficult to observe, as the stationary interferences are very prominent in the red. Between D and E, however, the agreement is as close as the method warrants.

6. *Conclusion.*—The above results, taken as a whole, bear out the surmise that it must be possible to determine the refraction of solid and liquid media by means of displacement interferometry, with any degree of accuracy desirable, depending ultimately on the length of the refracting column employed. The centre of ellipses is never lost but may be brought back to the fiducial Fraunhofer line, if the micrometer screw is sufficiently long and the end faces of the medium are plane parallel. If the latter is not the case, and the angle of wedge is not too large, the discrepancy may be corrected by compensation. For this purpose the distant mirror N (not the one at the micrometer M and controlling the beam passing through the medium) is to be rotated to restore the ellipses.

The coefficient $d\mu/d\lambda$ may be obtained by the same method with an adequate degree of accuracy, by using successive Fraunhofer lines. In the case of work of precision, the Cauchy equation as far as the fourth power of wave-length is necessary, and three Fraunhofer lines are needed to determine the two essential constants. For this purpose it is immaterial whether the plate is slightly wedge-shaped or not.

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* See Landolt and Börnstein's Tables.

If the optical constants of doubly refracting media are to be observed, the plates are to be mounted for rotation around an axis parallel to the slit and passing symmetrically between the faces. Otherwise the wedge effect is liable to produce excessive distortion in the results. If columns are to be used, plane parallel faces are to be cut at a definite angle to the optic axes, as the columns cannot be rotated.

The position of minimum thickness of the plate or crystal may be recognized by the aid of two rotations, at right angles to each other, and the reversal of motion of the interference rings. It is thus easy to place the axis of rotation at right angles to the beam.

The interferometer used in the above experiments was an improvised apparatus, made of 1/4 inch gas-pipe through which water continually circulated. The angle between the component or interfering beams being but 30°, or less, the micrometer was sufficiently close to the observing telescope to admit of easy manipulation. The arms have since been elongated to over 1 metre in length each, and the available free depth below the beam is 15 centimetres. There seems to be no difficulty of increasing these dimensions in any degree. In spite of the lightness of the apparatus, tremor of ellipses does not seriously hamper the observations. Suppose now a glass column 1 metre long with plane parallel end faces is placed in one of the beams. The micrometer displacement which restores the centre of ellipses to the fiducial sodium line will be of the order of 50 centimetres, measurable, so far as the interferences are concerned, to 5×10^{-5} centimetre. Hence $\mu-1$ must be measurable with an accuracy of 1 part in a million.

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LXXXIX. *On the Shape of the Capillary Surface formed by the External Contact of a Liquid with a Cylinder of Large Radius.* *By* ALLAN FERGUSON, *B.Sc.* (*Lond.*), *Assistant Lecturer in Physics in the University College of North Wales, Bangor*[*].

THE following analysis is an attempt to find an approximate value for the first integral of the differential equation of the capillary surface formed when a cylinder is dipped vertically into a liquid. The writer's attention has been recently devoted to the photography of the capillary surface formed by pendent drops*, and it seemed possible that photographs of the meridional curve of the capillary surface in external contact with a cylinder might give useful information as to the angle of contact of a liquid and solid. A few preliminary experiments have been made which indicate the feasibility of the formulæ developed below. The present paper will, however, be devoted to the discussion of these formulæ, leaving the experimental results for future presentation.

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[*] Communicated by Prof. E. Taylor Jones.

In the paper referred to above, several approximations to the outline of the capillary curve have been discussed. To these may be added the equations

$$a^2=q^2+\frac{2qa^2}{\mu}-\frac{a^2}{3e}(2\sqrt{2}-1),$$

and

$$a=\frac{k}{\sqrt{2}\cos\frac{\omega}{2}}+\frac{a^2}{\mu\sqrt{2}\cos\frac{\omega}{2}}-\frac{a^2}{3l\sqrt{2}\cos^2\frac{\omega}{2}}\left(1-\sin^3\frac{\omega}{2}\right),$$

originally due to Poisson†, and modified by Magie‡. All of them have reference to the capillary surfaces formed by drops, pendent or sessile; the writer has not found any discussion of the particular capillary curve which forms the subject of the present paper.

In the discussion which follows it is important to bear in mind that the angle of contact of the liquid and solid is assumed to be acute; that the radius (r) of the cylinder is assumed to be large in comparison with the other quantities to be measured; and in the discussion of the signs of the various quantities involved—a point which has an important bearing on the shape of the resulting formulæ—the signs will always be chosen in accordance with the diagram given in fig. 1 below.

Let Y′ O′ O″ Y″ be the trace of the cylindrical surface, of which OY is the axis, immersed in the fluid. Let OY be vertical and OX any horizontal line drawn in the "level" surface of the fluid.

The capillary surface will be a surface of revolution about

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* Phil. Mag. March 1912.

† *Nouvelle Théorie,* p. 217.

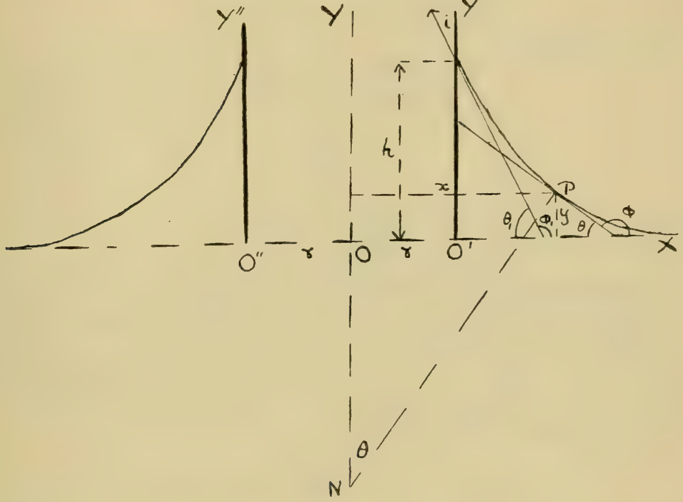
‡ Phil. Mag. vol. xxvi. (1888).

OY, and at any point P (x, y) the equation to the surface is

$$\frac{1}{R_1}+\frac{1}{R_2}=\frac{y}{a^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(i.)}$$

where $a^2 \equiv \frac{T}{g\rho}$, and a is therefore of the dimensions of a

Fig. 1.



length. R_1 and R_2, the principal radii of curvature at P, are given by

$$R_1=\frac{(1+y_1{}^2)^{3/2}}{y_2},$$

and

$$R_2=PN=\frac{x}{\sin\theta}=\frac{x\sqrt{1+y_1{}^2}}{-y_1},$$

remembering that

$$\tan\theta=-\tan\phi=-y_1.$$

Hence, substituting in (i.) and clearing of fractions we have for the differential equation of the meridional curve

$$a^2xy_2-a^2y_1(1+y_1{}^2)=xy(1+y_1{}^2)^{3/2},$$

or

$$a^2x\frac{dp}{dx}-a^2p(1+p^2)=xy(1+p^2)^{3/2}. \quad . \quad . \quad . \quad . \qquad \text{(ii.)}$$

Referred to parallel axes through O′ as origin, (ii.) becomes

$$a^2(x-r)\frac{dp}{dx}-a^2p(1+p^2)=(x-r)y(1+p^2)^{3/2}, \quad . \quad \text{(iii.)}$$

or

$$\frac{a^2x}{r}\frac{dp}{dx}-a^2\frac{dp}{dx}-\frac{a^2p}{r}(1+p^2)=\frac{xy}{r}(1+p^2)^{3/2}-y(1+p^2)^{3/2}, \text{(iv.)}$$

giving when $r=\infty$

$$a^2\frac{dp}{dx}=y(1+p^2)^{3/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

or

$$\frac{y}{a^2}=\frac{1}{\mathrm{R}_1},$$

which is obviously the correct equation to the capillary surface in contact with a plane wall.

To obtain an approximate solution of (iv.) on the assumption that r is large, take the value of $\frac{dp}{dx}$ in (v.)—which is exactly true when r is infinite—and substitute in the first term on the left-hand side of (iv.), which is a small term. We thus obtain

$$a^2\frac{dp}{dx}+\frac{a^2p}{r}(1+p^2)=y(1+p^2)^{3/2},$$

or putting $\frac{dp}{dx}=p\cdot\frac{dp}{dy}$,

$$\frac{dp}{dy}+\frac{1+p^2}{r}=\frac{(1+p^2)^{3/2}}{a^2p}y. \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

Again, if r be infinite, (vi.) becomes

$$\frac{dp}{dy}=\frac{(1+p^2)^{3/2}}{a^2p}y,$$

giving on integration,

$$y^2=2a^2\left(1-\frac{1}{\sqrt{1+p^2}}\right), \quad . \quad . \quad . \quad . \quad \text{(vii.)}$$

the integration constant being obtained from the fact that y and p vanish together.

Also, when $y=h$, $p=\tan\phi_1=-\cot i$ (*vide* fig. 1) giving

$$h^2=2a^2(1-\sin i), \quad . \quad . \quad . \quad . \quad . \quad \text{(viii.)}$$

the usual expression for the height to which a liquid rises against a plane wall.

Now write (vi.) in the form

$$\frac{a^2p}{(1+p^2)^{3/2}}\frac{dp}{dy}+\frac{a^2}{r}\cdot\frac{p}{\sqrt{1+p^2}}=y, \quad . \quad . \quad . \quad \text{(ix.)}$$

and substitute in the second term on the left-hand side of (ix.) the value of $\frac{p}{\sqrt{1+p^2}}$ given by (vii.).

We have at once from (vii.)

$$p=\pm y\frac{\sqrt{4a^2-y^2}}{2a^2-y^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(x.)}$$

and if the angle of contact be acute y^2 is always less than $2a^2$ (*vide* equation (viii.)); also from fig. 1, p is continuously negative. Hence in (x.) above, the negative sign must be chosen, and

$$\frac{p}{\sqrt{1+p^2}}=-\frac{y\sqrt{4a^2-y^2}}{2a^2}.$$

Substituting in (ix.) we have

$$\frac{a^2pdp}{(1+p^2)^{3/2}}=\left(y+\frac{y\sqrt{4a^2-y^2}}{2r}\right)dy,$$

which, integrating, and remembering that when $y=0, p=0$, gives

$$a^2\left(1-\frac{1}{\sqrt{1+p^2}}\right)-\frac{4a^3}{3r}=\frac{y^2}{2}-\frac{1}{6r}(4a^2-y^2)^{3/2}. \quad \text{(x. }a\text{)}$$

As before, when $y=h, p=-\cot i$, giving

$$a^2(1-\sin i)-\frac{4a^3}{3r}=\frac{h^2}{2}-\frac{4a^3}{3r}\left(1-\frac{h^2}{4a^2}\right)^{3/2}. \quad . \quad . \quad \text{(xi.)}$$

In this equation, h, r, and a^2 are capable of experimental determination, and i can therefore be calculated.

Equation (xi.) can be put into a very simple form by expanding the quantity under the radical sign, and neglecting

$\frac{h^4}{16a^4}$ and higher powers; the expansion is legitimate, as h^2 is always less than $2a^2$ for acute angles of contact. This gives at once

$$2a^2(1-\sin i)=h^2\left(1+\frac{a}{r}\right),$$

or, if h_0 be the height to which the liquid rises against a *plane* wall, then, very approximately,

$$h^2=h_0^2\left(1-\frac{a}{r}\right).$$

Equation (xi.) should, however, always be used in computing $\sin i$ from numerical data.

A solution of (vi.) in a different form can be obtained in the following manner.

Putting $p=\tan\phi$, substituting, and taking, for reasons similar to those already given, the negative sign in extracting the square root of $\sec^6\phi$, (vi.) becomes

$$\frac{d\phi}{dy}+\frac{1}{r}=-\frac{4}{a^2\sin\phi}. \quad . \quad . \quad . \quad . \quad \text{(xii.)}$$

Putting the right-hand side of (xii.) equal to zero, and integrating,

$$r\phi=-y+c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiii.)}$$

Assuming c to be a function of y, as in the ordinary method of variation of parameters,

$$\frac{d\phi}{dy}=\frac{1}{r}\frac{dc}{dy}-\frac{1}{r}; \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

substituting in (xii.) the values of c and $\frac{d\phi}{dy}$ given by (xiii.) and (xiv.) we have

$$\frac{1}{r}\frac{dc}{dy}=-\frac{y}{a^2\sin\frac{c-y}{r}},$$

or

$$ydy=-\frac{a^2}{r}\sin\frac{c-y}{r}dc,$$

$$=-\left(\frac{a^2}{r}\sin\frac{c}{r}-\frac{y}{r^2}\cos\frac{c}{r}\right)dc.$$

If we neglect the term involving $\frac{y}{r^2}$ on the right-hand side of the above equation, we then have

$$ydy = -\frac{a^2}{r}\sin\frac{c}{r}\,.\,dc, \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

giving on integration

$$c = r\cos^{-1}\frac{y^2-c_1}{2a^2}.$$

Substituting in (xiii.), we obtain

$$\frac{y^2-c_1}{2a^2} = \cos\left(\phi+\frac{y}{r}\right),$$

and when $y=0$, $\phi=\pi$, giving

$$\frac{y^2-2a^2}{2a^2} = \cos\left(\phi+\frac{y}{r}\right) = \cos\left(\tan^{-1}p+\frac{y}{r}\right). \quad \text{(xvi.)}$$

As before, when $y=h$, $p=-\cot i$, and therefore

$$\frac{2a^2-h^2}{2a^2} = \sin\left(i+\frac{h}{r}\right), \quad . \quad . \quad . \quad \text{(xvii.)}$$

a convenient equation to determine i.

Equations (xvii.) and (xi.) represent approximations of different orders of accuracy, of which (xi.) is the closer. The neglect of the term involving $\frac{y}{r^2}$ in forming equation (xv.) is evidently of a lower order of accuracy than the processes which result in equation (xi.). The difference between the two results can readily be shown by computing the value of $\frac{2a^2-h^2}{2a^2}$ as given for the two equations.

If we take, for simplicity, a liquid of zero contact-angle, a simple calculation shows that

$$\left(\frac{2a^2-h^2}{2a^2}\right)_{\text{xvii}} - \left(\frac{2a^2-h^2}{2a^2}\right)_{\text{xi}}$$

$$= \frac{h}{r}\left(1-\frac{h}{2a}\right),$$

a small difference which becomes less important as r increases. The preliminary experiments which have been carried out are in agreement with this result. The approximation of equation (xvii.) is specially convenient, as a knowledge of the slope of the tangent at any point enables a^2—and therefore the surface-tension—to be calculated by means of the simple equation (xvi.), with much greater ease than would be the case were equation (x. a) to be used.

A knowledge of a^2 is, of course, necessary before i can be computed. This can be obtained from a photograph of the capillary curve by means of equation (xvi.) above, or directly by measuring, at the same time that the photograph is taken, the weight (mg) necessary to balance the pull due to surface-tension on a vertical plate of known perimeter p, just touching the surface of the liquid. We then have

$$p\mathrm{T}\cos i = mg,$$

or

$$a^2 \cos i = \frac{m}{p\rho} = k, \quad . \quad . \quad . \quad . \quad \text{(xviii.)}$$

where k is a known quantity. We can now eliminate a^2 between (xviii.) and (xi.), or (xviii.) and (xvii.). The first elimination gives a cubic for i; the second gives a much simpler form, thus:—

Substituting for a^2 in (xvii.), we have

$$1 - \frac{h^2 \cos i}{2k} = \sin\left(i + \frac{h}{r}\right),$$

$$= \sin i + \frac{h}{r}\cos i,$$

whence

$$\sin i + \mathrm{A}\cos i - 1 = 0,$$

where

$$\mathrm{A} = \frac{h}{r} + \frac{h^2}{2k}.$$

This gives finally

$$\cos i = \frac{2\mathrm{A}}{\mathrm{A}^2 + 1},$$

giving i in terms of known quantities.

Having determined $\cos i$, equation (xviii.) gives a^2, or T.

In a future communication the writer hopes to give the results of experiments based on the formulæ detailed above.

University College of North Wales, Bangor,
June 1912.

XC. *Studies in the Photometry of Lights of Different Colours.—IV. The Addition of Luminosities of Different Colour.* By HERBERT E. IVES *.

A WELL-NIGH indispensable requirement of a method of measurement is that its renderings shall conform to two geometrical axioms. The first of these is that things equal to the same thing shall be equal to each other ; the second, that the whole shall be equal to the sum of its parts.

In the majority of measurements performed in the physical laboratory the quantities dealt with are of such nature that conformity to these axioms is unquestioned. Among these measurements fall those of illuminations of identical colour and quality. But when the condition of complete identity of quality in the compared quantities is departed from, as is the case in the photometry of lights of different colour, it is unsafe to assume that these axiomatic relations hold. This paper discusses the methods of heterochromatic photometry from the standpoint of these axioms. It is shown that only one method—the flicker method—strictly conforms to the requirements in question.

As to the first requirement, that things measuring equal to the same thing shall measure equal to each other, the subject matter of the previous papers of this series gives complete information. By the methods of visual acuity and critical frequency this is so, from the nature of the measuring process, in which no real comparison source—whose character might be varied—exists. In the two remaining methods—equality of brightness and flicker—the fulfilment of this requirement reduces to this—that no change in the character of the reference standard shall affect the *relative* brightness of the different coloured lights under measurement. In the case of spectral luminosity curves this means that the shape of the curve must not be altered by a change in the reference standard. In the last preceding paper of this series it was shown that by the equality of brightness method various distortions of the spectral luminosity curves may be expected upon changing the hue of the reference standard. By the flicker method such changes do not take place. Therefore the first requirement mentioned above is met by the flicker method, but not by the equality of brightness method. Two different equality of brightness methods must, however, be distinguished, the ordinary one, where large hue differences are under comparison, and another, where by steps of small hue difference the psychological element of appraisement is eliminated. As was shown by the last paper, the latter procedure gives results identical to the flicker method. In the present paper, when equality of brightness is mentioned, the straightforward method of comparison as usually carried out with large hue differences will be meant.

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* Communicated by the Author.

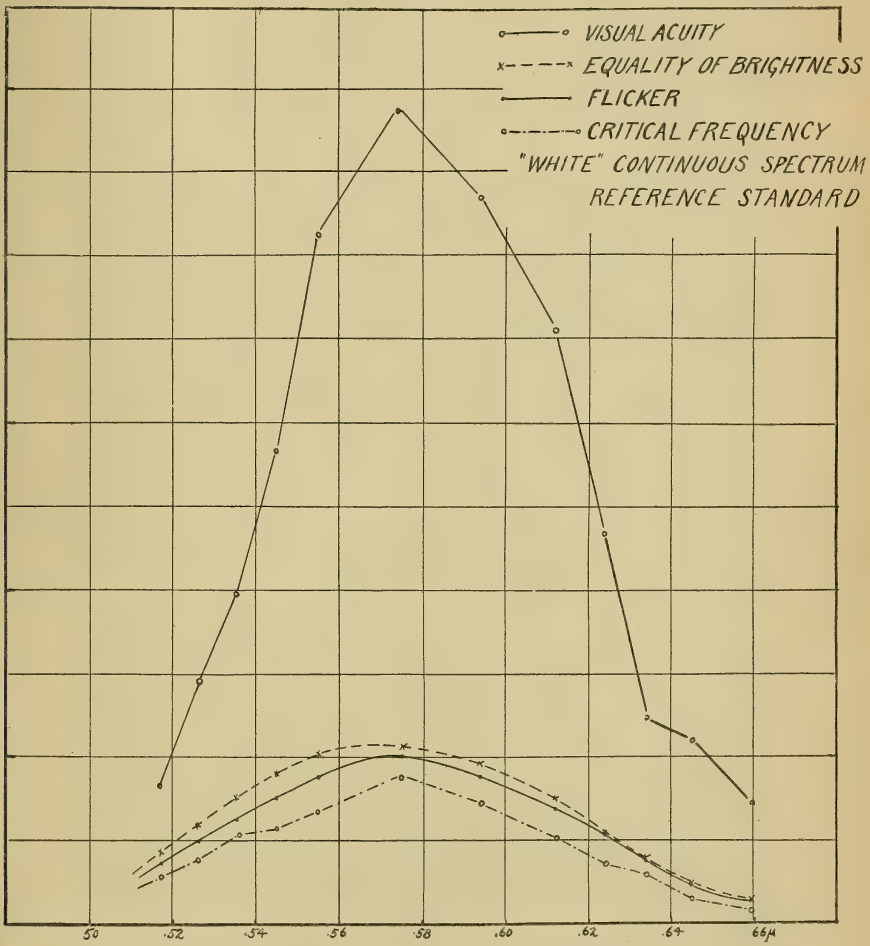
As to the second requirement—the summational one—it is to be borne in mind that while this presupposes the first one fulfilled, it may fail even with that holding. The process of physical summation may introduce factors which are not present or magnify ones not significant in the separate parts. An instance of this is given below. It is to be noted further that certain differences may exist in the results of two methods without any clash with this second requirement. Speaking in terms of spectral luminosity curves, this means that the curves by different methods may differ in the position of their maxima, and may show different directions of change with variation of illumination, but if they maintain their areas the same may all conform to the requirement in question. If, however, the areas of the luminosity curves are different, then the sum of the parts cannot equal the whole by all the methods under test. This is obvious when one imagines the luminosity curve under measurement to be that of a source identical with the comparison standard. If at the end of the spectral measurement the dispersed light is recombined, then, being identical in quality with the comparison standard, it must measure the same by all methods of measurement. If by one method of measurement this physical summation agrees with the arithmetical summation, derived through the area measurement, it cannot agree with others giving different areas.

As has been noted from time to time in these papers, curves of different area are obtained by the different methods of coloured light photometry. A striking example of this is given in fig. 1, where are four luminosity curves obtained at one sitting by the methods of visual acuity, critical frequency, equality of brightness and flicker. While they differ little in general shape and position of maxima, the enormous differences in area illustrate forcibly the error fallen into by assuming these methods identical on the basis of the similarity in shape of curves obtained by different observers. The most startling curve is the visual acuity one. This was obtained by the use of a test object consisting of a fine line grating placed over the telescope lens. Its area is five times that of its nearest neighbour, which latter differs only by a fractional part from the other two.

The enormous area of the visual acuity curve is at once explainable as due to the chromatic aberration of the eye.

Fig. 1.

Simultaneously Obtained Spectral Luminosity Curves by four Photometric Methods.



It has been shown by Bell * and by Luckiesh †, in work published since the first of these papers was written, that the defining power of the eye is much greater for monochromatic light than for complex light of the same hue. It may thus

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* L. Bell, Elec. World, vol. lvii. p. 1163 (1911).

† M. Luckiesh, Elec. World, vol. lviii. p. 450 (1911).

easily happen—in the case of a purple composed of red and blue light—that increase of illumination reduces the detail-revealing power of the eye, although for the component parts of the acting light the normal relation between visual acuity and brightness holds. The visual acuity curve of fig. 1 is therefore analysable as a combination of the acuity-brightness relation and what may be termed a *quality factor*. It is a perfect example of a method of measurement in which axiom 1 is valid, but not axiom 2. Needless to say, the existence of such a quality factor effectually disposes of the method of visual acuity as a method of measuring *brightness*.

The differences between the remaining three methods are probably due to more obscure psychological causes. In the case of critical frequency the ease with which area differences may be produced has been pointed out. The manner in which the equality of brightness curves are disturbed by varying the comparison standard is sufficient reason for regarding without surprise the differences which have been found between these areas and those by the flicker method.

The crucial test of axiom 2 appears to be, in the light of all previous work, reduced to its test by the flicker method. Such tests have been made by Whitman [*], and later by Tufts [†]. Since the latter's was more complete, the experimental test which is described below was modelled upon his, with, however, certain very essential modifications. A brief account of his experiment is necessary.

Two identical incandescent lamps were chosen, one so placed as to illuminate a white surface before the slit of a spectrometer, the other so placed as to illuminate a rotating sector in front of the telescope lens. The latter lamp was placed on a photometer track so as to be movable. The slit-width was held constant and the brightness of the spectrum measured at several points by the flicker method. At the end the *prism was removed*, and the brightness of the total light through the spectrometer was measured against the movable lamp. This was found to be within a few per cent. the same as that indicated by the area of the luminosity curve.

Further experiments showed the area of the luminosity curve to be unaltered by observing through a coloured glass, as it should not be if axiom 2 holds. When, however, a deep cobalt blue glass was used a large discrepancy was found. Certain other observers, who were less red-sensitive

[*] Whitman, Phys. Rev. iii. p. 241 (1896).

[†] Tufts, Phys. Rev. xxv. p. 433 (1907).

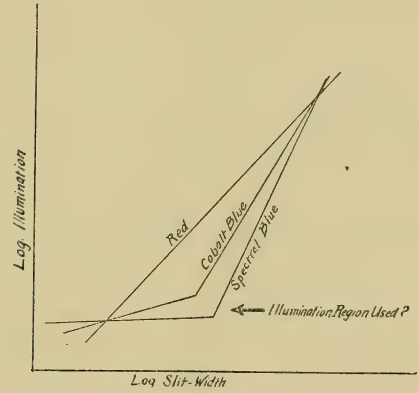
than Tufts, showed a discrepancy in the same direction even with white light.

The points to which attention should be directed here are, 1st, that the conditions of illumination and field-size are not stated, nor was the illumination constant. Instead of taking portions of the spectrum of equal brightness, equal slit-widths were taken, with consequent low illumination at the red and blue ends. 2nd, there is no mention of correction for the light lost by absorption and reflexion in the prism. It is hard to imagine that this correction was not made, but the test is inconclusive as long as this is in doubt.

With regard to the peculiar discrepancy with the deep cobalt glass, this can be explained, qualitatively at least, by the results of paper II. of this series. Bearing in mind that the effect of this screen over the eye is to reduce the illumination excessively, it is quite possible that the spectral blue measurements fell in the region indicated by the arrow in the (slit-width) diagram sketched in fig. 2, in a region where the law of the flicker photometer changes (see paper II. of this series). The result of this would be the effect found by Tufts. However, these low illumination effects, interesting as they are in connexion with the theory of colour vision, cannot be held of primary interest in practical photometry.

Fig. 2.

Suggested Explanation of Anomalous Results of Tufts.



A repetition of this experiment is here described, in which the undesirable features of Tufts' experiments are eliminated. Because this work is intended primarily for application to practical photometry no repetition is made of the low illumination tests, nor tests on observers of abnormal colour vision.

The apparatus used is that employed in the previous investigations described in this series with certain modifications. An important feature is a special slit, made with both jaws movable. One is moved by the divided head as before (adjustable edge) ; the other is free and may be brought into contact with the first by merely sliding in its ways. The method of use is to leave the prism fixed throughout the experiment ; the adjustable edge of the slit is placed in a position corresponding to the ultra-violet, the free edge brought into contact with it. The adjustable edge is then moved by the divided head until, by the flicker criterion, a piece of the spectrum is transmitted equal in brightness to the comparison standard. The free edge is then brought up into contact with the adjustable edge and another piece of the spectrum of the same brightness exposed by moving the latter. In addition to this slit another means of varying the amount of spectral light is furnished by a variable neutral tint screen * between the light source and the ground glass over the slit. This is used at the end of the spectrum, where the last portion of spectral light consists of the whole remainder of the spectrum and cannot be varied in brightness by slit-width variation. (This screen can of course be used at any point if so desired in place of slit-width variation, it being only necessary to take slit-widths of suitable size so as to give approximately the same amount of light.) At the end of the spectral measurements the free jaw is drawn back to its original position, whereupon the eye-slit receives the whole spectrum which it has before received in parts. The prism used in this test was a special constant dispersion, constant deviation type, made by A. Hilger. It gives a considerably shorter spectrum than that furnished by the regular crown glass prism used before.

A new form of flicker photometer was used in place of the rotating disk of the previous work. This consists of a first surface metal mirror on an oscillating lever. The mirror was made by coating a glass plate with platinum by cathode discharge, then cutting the glass with a diamond. The edge where the glass breaks is almost invisible in the photometer field †. The other end of the lever is driven by a link motion attached to the speed counter axis and having a 1-inch stroke.

This mirror device gives a close approximation to a perfect flicker photometer. With regard to the question of

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* "A Variable Absorption Screen," Ives, Elec. World, March 16, 1912.

† Pfund, Johns Hopkins Univ. Circular, vol. iv. 1906, pp. 20–22.

perfection in flicker photometers, a word may be said. Some experimenters have thought they found differences in the results with the flicker photometer when it was operated at different speeds. As a matter of fact there is only one speed for such a photometer, namely, that which just causes colour flicker to disappear. Any greater speed causes a decrease of sensibility. Now as the colour difference is decreased a decrease in speed and an increase in sensibility are made possible. If there is no difference in colour, the speed drops to *zero*. In other words, *for lights of the same colour the flicker photometer approaches as its limiting case the equality photometer*. In the instrument now described this is proved to be literally so. By proper choice of voltages on the test and comparison lamp, and by slightly tinging the light from the latter by letting it fall upon a flashed opal glass over which is laid four thicknesses of lantern-slide cover-glass, the total spectral light, obtained from the wide slit, and the comparison standard light, are identical in appearance. The speed for greatest sensibility is as it should be, *zero*.

Another detail of some importance is that in measuring the total light through the prism a neutral tint screen * is placed over the slit, of such transmission that it reduces this light to approximately the same brightness as the comparison standard, the exact setting being made by means of the variable neutral tint screen before mentioned. The object of this is to have all the measurements carried on at the same brightness, although since this final measurement is of lights of the same colour it is not perhaps absolutely necessary.

It may fairly be claimed for this arrangement of apparatus that physically the whole is exactly the sum of the parts. There is no measurement of areas; all scattered light is present exactly in the same manner in the fractional and total light measurements; there are no instrumental changes for which correction need be made, such as the removal of the prism in Tufts' experiment.

Three sets of measurements were made. For each an illumination of 300 I.U. held; the field was 2° diameter, and surrounded by a large bright area (25° diameter). Two sets were made by the writer, whose luminosity curve lies nearly at the blue extreme of the observers previously examined, one set by Dr. P. W. Cobb whose luminosity curve lies at the red extreme.

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* "A Form of Neutral Tint Absorbing Screen," H. E. Ives & M. Luckiesh, Phys. Rev. May 1911.

The results were as follows :—

	By parts.	Total.
H.E.I. I.........	691	695
H.E.I. II.........	742	743
P.W.C. I.........	773	785

(Slight changes in the position of the variable screen and comparison lamp cause the different magnitude of the results in the arbitrary units given.) The greatest difference is in the case of the less practised observer and amounts to $1\frac{1}{2}$ per cent. This lies within the range of his errors of setting.

The conclusion is drawn that under the conditions of high illumination and small field size specified, the arithmetical sum of the parts as measured agrees with the measured value of the whole, by the flicker method, for observers of normal colour vision.

With the proof of this property of the flicker method of photometry is concluded the set of tests which were planned at the beginning of the investigation. A general summary of the characteristics of the flicker method follows :—

1. It surpasses all other photometric methods in sensibility and reproducibility in the presence of colour difference.
2. It agrees at high illuminations with the equality of brightness method, when the latter is freed from the psychological uncertainties inherent in its use.
3. It measures at high illuminations what may fairly be termed the true brightness.
4. Brightnesses measuring equal to the same measure equal to each other and the sum of the measurements of the parts is equal to the measurement of the whole.

In the opinion of the writer the flicker photometer should be adopted as the standard instrument for making heterochromatic comparisons in the standardizing laboratory. Before, however, this can be done, the standard conditions of illumination and field-size should be agreed upon, and, most important of all, the normal luminosity curve of the eye should be determined from observations on a large number of individuals. This done, not only will it be possible to determine which individuals should be chosen to make such comparisons, but also, in virtue of the various qualities of the flicker photometer, it will be possible to correct to normal the results of any observer whose luminosity curve is known. The next paper of this series will be devoted to a discussion of standard conditions for heterochromatic photometry and give values for the luminosity curve of the average eye.

Attention may here be called to the fact that the solution of the problem of heterochromatic photometry clears the way for the establishment of a rational primary standard of light flux, namely, a certain rate of flow of radiant energy of maximum luminous efficiency*. It is hoped to use the results of this study of coloured light photometry in a determination of the luminous equivalent of the most efficient radiation, a quantity which, in accordance with the above suggestion, is identified with the rational primary standard of light.

Physical Laboratory,
National Electric Lamp Association,
Cleveland, Ohio.
June 1912.

XCI. *Studies in the Photometry of Lights of Different Colours.—V. The Spectral Luminosity Curve of the Average Eye.*

By Herbert E. Ives †.

ACCORDING to the results published in previous papers of this series the flicker photometer, under certain conditions, conforms most nearly of all photometric methods to the requirements for a method of heterochromatic photometry. Granting its adoption as the standard instrument for this kind of photometry, there remain to be determined the characteristics of the average human eye. Given the satisfactory photometric method, and the standard eye to use it, the measurement of the relative brightness of differently coloured lights becomes a definite thing.

The present paper gives the result of an experimental determination of the mean luminosity curve of eighteen observers, sixteen men and two women, aged from 18 to 40 years. Since none of these were colour-blind or possessed any known abnormalities of vision, the mean of their values may be considered as that of an average normal eye. The number of observers is sufficiently great to warrant the belief that the mean thus obtained is sufficiently near the absolute mean eye for all practical purposes.

The conditions holding during the measurements, the reason for their choice, the details of the work, together with the results, are discussed below under the several headings.

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* "Energy Standards of Luminous Intensity," H. E. Ives, Trans. Ill. Eng. Soc. March 1911; "Luminous Efficiency," Elec. World, June 15, 1911.

† Communicated by the Author.

Photometric Conditions.

Flicker Photometer.—The flicker photometer was chosen for reasons made clear in the previous papers of this series. It possesses the greatest sensibility, its results are most reproducible; by its use, things measured equal to the same thing measure equal to each other, and the sum of the measurements of the parts equals the measurement of the whole.

Illumination.—An illumination of 25 metre candles was chosen since, by the means described below, this was found to correspond closely to the high illumination at which the results of the flicker and equality of brightness methods become the same. This is a practicable illumination for the usual laboratory light sources and photometers; it corresponds to a comfortable working illumination for reading, &c., and the changes in visual colour sensitiveness on going to the still higher illuminations common by daylight are probably small, perhaps negligibly so.

Size of Photometric Field.—A photometric field of 2° diameter was selected; that is, the smallest field used in the previous work, for the reason that the changes in the luminosity curve due to changes in illumination are least with the small field. This field size, together with the high order of illumination chosen, would permit considerable latitude in the illumination without appreciable effect on the result.

Bright Surrounding Field.—The small photometric field was surrounded by a bright field of about 25° diameter, maintained at approximately the same brightness as the photometric field. This bright area, although previously not found to affect the results of the flicker photometer to an extent greater than the errors of measurement, was used for the greater comfort which it gives when observing with a small field. It is not an essential part of the scheme of measurement, but for the sake of complete uniformity should be used always, if at all.

Apparatus.

The apparatus was the same as in the previous work. A Hilger spectrometer with a $\frac{1}{2} \times 2$ mm. slit in place of the eyepiece; the light from the comparison lamp (4 watt carbon), after falling upon a magnesium oxide surface, is reflected into the spectrometer telescope from a first surface platinized glass mirror arranged to oscillate and so form a flicker photometer; the diaphragm which limits the size of the field is white and is illuminated by auxiliary carbon lamps. The speed counter, slit mechanism, &c., have previously been described in detail. The light source whose spectrum was measured was, as before, a tungsten lamp; the details of its use are given below.

Details of Measurements.

Energy Distribution in Spectrum of Light Source.—The spectral luminosity curve which is desired is that of a known energy distribution, from which the luminosity curve of any other distribution may be derived. For convenience it is desirable to give the results for an equal energy spectrum. Were it feasible to measure the intensity of radiation directly at the eye-slit this would be the ideal measurement, since it would at once eliminate the determination of various instrument corrections. In the present investigation this was not considered practicable, so measurements were made on a set of four frosted bulb tungsten lamps whose energy distribution was determined as follows:—All four lamps (previously seasoned) were carefully colour-matched on a photometer against a tungsten standard of 1·15 watts per mean horizontal candle-power. Immediately before and immediately after the use of each lamp on the flicker spectrometer it was measured on a spectrophotometer (substitution method) against a tungsten lamp which had previously been measured against a black body of known temperature *. This latter lamp had a visual energy distribution corresponding to a black body at 2295° abs. The frosted lamps were compared with it at four points in the spectrum. The distribution for a black body,

$$J_\lambda = c_1 \lambda^{-5} e^{-\frac{14500}{\lambda T}},$$

was plotted as a straight line in the form

$$\log \frac{J_\lambda}{c\lambda^{-5}} = -\frac{14500}{\lambda T} \cdot \log_{10} e.$$

The spectrophotometer ratios were plotted (in logarithmic units) against this straight line; through these points another straight line could be drawn if the new energy distribution corresponded to another black body colour, as is pretty well established. This was found to be the case, and from the slope of this line the equivalent black body temperature of 2360° abs. was found for the lamp in question. The distribution calculated for this temperature was in turn corrected for the selective absorption of the prism, ground glass, and lenses, determined spectrophotometrically, as well as for the dispersion of the prism. Applying the final value of the energy distribution to the readings, the results are obtained for an equal energy normal spectrum.

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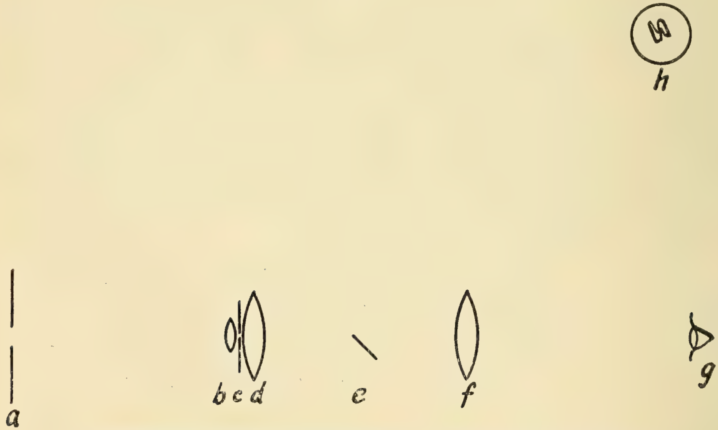
* This standard of black body distribution was obtained and has been maintained for this Laboratory by Dr. E. P. Hyde.

Elimination of Artificial Pupil.—In all the previous work an artificial pupil was used and the results were given in terms of metre-candles illumination as viewed through this 1 sq. mm. aperture. In working with a spectrometer the use of a small eye-slit is practically imperative. But in practical photometry an artificial pupil of this size would necessitate working at illuminations too high to be practicable with present illuminants if one had to attain the retinal illumination called for by the investigation here described. Were the pupils of all observers of the same size under the same conditions, a reduction factor might be obtained so that the luminosity curve could be found with the artificial pupil and used for a corresponding illumination with the natural pupil. Such, however, is not the case.

Fig. 1.



Arrangement for securing the same working illumination for all observers.

In view of these facts it was considered advisable in the present research to have all curves made for a normal pupil illumination. In order to accomplish this, the arrangement shown in fig. 1 was adopted. *a* is the diaphragm limiting the photometric field; *b* is a small spectacle lens of focal length *ab*; *c* is the eye-slit or artificial pupil; *d* is a lens of focal length *de*; *e* is a magnesium oxide surface illuminated by the lamp *h*; *f* is a lens of focal length *ef*. At *g* is formed an image of the slit *c*; the eye placed here sees the image of the diaphragm *a* in the same plane as the edge of *e*, and by moving the comparison lamp the field may be made of the brightness of *e*. The auxiliary lenses are then removed, proper correction made for the loss of light caused by the various lenses, and the slit *c* used as before.

A test of the illumination used in the previous investigation of the series—which in turn had been chosen to be in the region where the flicker and equality of brightness method had been found to agree, and where large and small field agree, viz. 300 "illumination units"—showed that for the writer's eye it was close to 25 metre candles. As this was desirable from various standpoints, it was taken as the constant illumination on *e*. Each observer was required to find the artificial pupil illumination corresponding to 25 metre candles normal pupil, and his luminosity curve was then obtained at that illumination. In this way the results all apply to the standard illumination under ordinary photometric conditions. It was found that the highest illumination used was about twice the lowest. This range would make no noticeable difference in the luminosity curve with the illumination and field size used.

Details of Procedure.—The measurements of brightness were carried out as in the previous work, by finding the slit openings to match a constant comparison illumination. The zero of the slit was found as follows:—By means of colour screens the light of the comparison lamp was made to match a certain wave-length ($\cdot 59\,\mu$); then a series of three neutral tint screens of known transmission were placed successively over the comparison lamp side and the slit width obtained for photometric match. These values when plotted against the transmissions give a straight line passing through the effective zero. This method proved very satisfactory.

The calibration for wave-length was provided for by having the eye-slit adjustable sideways by a milled head; a helium tube was placed behind the tungsten lamp under measurement so that it could be turned on at intervals during the measurements and the setting of the drum checked. This prevented any instrumental drift.

A difficulty was met with in carrying the measurements down into the blue of the spectrum, namely, that the necessary slit widths became altogether too great for sensibility or accuracy. This difficulty was met by a compromise. For the measurements at $\cdot 50\,\mu$ and $\cdot 48\,\mu$ neutral tint screens of $\frac{1}{3}$ and $\frac{1}{5}$ transmission were used, so that these measurements were actually made at lower illuminations than the others. Since, however, the small field was used, and since even these illuminations are only just getting into the region of rapid change of luminosity curve shape (with large field), the errors will be small. They are also in just the opposite direction from the small errors due to the use of a wide slit in this spectral region.

The manner of taking observations was to start at the middle of the spectrum, then take observations back and forth, from red side to blue side, working toward the ends of the spectrum. This was found a desirable procedure, because it gave the observers a chance to obtain practice on the measurements with least colour-difference. At the end the first two or three readings were repeated until a close check was found. With some observers a check was obtained on the first wave-length, while with others there was a difference of several per cent. until the second or third wave-length. The mean of both sets was taken where a difference was found. Such differences are probably to be ascribed to lack of practice at the start.

All the scale-readings were made by an assistant, who watched voltages and held the speed constant.

Observers.—Of the eighteen observers, the majority had never used a flicker-photometer, while several had never before looked in a photometer of any kind. It is a striking point in favour of the flicker-photometer that its method of use can be acquired so quickly that there is little choice between the results of skilled and unskilled observers. The former differ from the latter chiefly in the greater speed with which they can make their readings. In instructing the inexperienced observers the procedure was compared to placing a blind man upon the side of a hill and asking him to find the top. As he finds his position relative to the summit only by stepping off in various directions, so the photometrist locates the minimum of flicker only by oscillating the illumination (slit) until each direction of motion increases the flicker. Standing still in either case is useless. The correct speed was determined as that which made the peak of the "hill" the sharpest.

Results.

The readings were first reduced to a normal equal energy spectrum as described above. The resultant curves were measured for area with a planimeter; then all were reduced to the same area and their mean taken. This seemed on the whole the fairest way to average the results, in view of the fact that owing to differences in shape certain curves would have less weight than others if plotted in terms of equal maxima or equality at any arbitrarily chosen wave-length. According to the results of the paper just previous in this series, the one thing common to all the curves would be their area when the comparison light and the light dispersed into a spectrum were identical.

The data of all observers are given in Table I., with their mean. Table II. gives the mean values in terms of the

Table I.

Normal Spectrum Luminosity Curves of Eighteen Observers.

Observer.	·481	·498	·518	·537	·556	·576	·595	·615	·635	·655 μ
1. P.W.C.	3·4	5·9	13·75	17·4	17·95	17·1	14·0	9·55	5·2	1·7
2. L.H.K.	4·15	7·1	15·5	18·7	18·6	16·5	12·2	7·5	3·65	1·15
3. E.J.E.	3·05	5·9	13·8	18·4	18·95	17·15	13·35	8·65	3·85	1·4
4. W.M.M.	3·6	7·4	15·2	18·45	19·05	16·65	12·45	7·75	3·8	1·15
5. M.D.C.	3·3	6·55	15·0	19·3	19·25	17·6	12·75	7·65	3·45	1·35
6. F.E.C.	2·3	5·05	13·9	17·9	19·1	17·55	14·3	9·4	4·95	1·95
7. M.L.I.	3·25	5·45	12·75	17·8	18·9	17·8	13·7	9·05	4·55	1·9
8. M.L.	3·3	7·7	14·2	18·7	19·8	18·2	12·3	7·3	3·45	1·35
9. H.A.R.	3·3	6·9	14·2	17·7	17·8	17·2	13·45	9·0	4·65	2·00
10. L.R.G.	2·65	6·95	15·9	19·55	19·9	17·2	12·3	7·7	2·9	0·9
11. M.M.	3·9	7·2	14·7	17·35	18·5	16·65	13·15	8·05	3·40	1·2
12. C.F.L.	2·7	5·45	13·2	18·1	18·7	17·5	14·15	9·2	4·9	1·6
13. A.J.S.	2·55	5·7	15·2	19·05	19·5	17·45	13·5	8·25	4·1	1·4
14. A.W.	1·6	3·65	12·65	16·9	18·05	18·25	15·6	11·05	5·85	2·3
15. H.H.M.	2·6	6·1	14·85	18·0	19·45	17·8	13·95	8·4	4·15	1·3
16. T.W.R.	3·7	7·4	14·15	19·9	20·1	17·5	12·0	6·7	3·15	1·25
17. H.E.I.	3·0	6·1	15·35	18·75	19·3	17·4	13·45	8·25	3·9	1·5
18. G.C.	2·15	5·2	12·6	18·8	19·4	17·1	14·0	9·3	5·0	1·6
Mean ……	3·03	6·2	14·55	18·38	19·03	17·47	13·36	8·52	4·16	1·5

Table II.

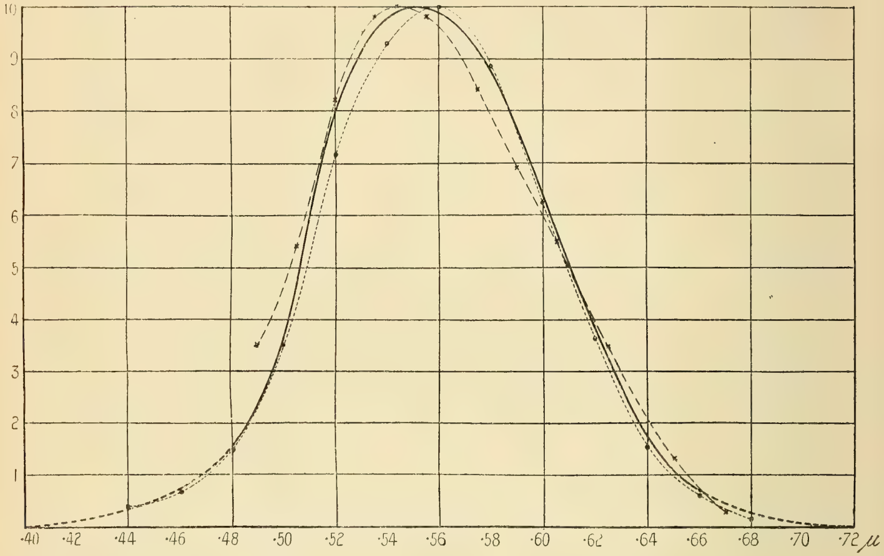
Relative Luminous Efficiencies of Spectral Radiations.

λ.			λ.		
·44 μ	·029		·57 μ	·948	
·45	·047		·58	·875	
·46	·073	*	·59	·763	
·47	·107		·60	·635	
·48	·154		·61	·509	
·49	·235		·62	·387	
·50	·363		·63	·272	
·51	·596		·64	·175	
·52	·794		·65	·104	
·53	·912		·66	·068	
·54	·977		·67	·044	*
·55	1·000		·68	·026	
·56	·990				

* Extrapolated.

maximum unity, constituting a table of relative luminous efficiencies of the spectral colours. In fig. 2 is plotted the

Fig. 2.



Average Normal Spectrum Luminosity Curve of Eighteen Observers at 25 metre candles illumination of MgO surface.

Dashed line — . . Kœnig's data, for his own eye, equality of brightness method.
Dotted line . . . . Thürmel's " " flicker method.

mean luminosity curve. Dotted in are the curves obtained by Kœnig [*], for his own eye (equality of brightness method), and by Thürmel [†] (flicker method, also for his own eye). The new curve, as it happens, is about midway in character between the two latter.

Fig. 3 gives all the eighteen curves, each plotted separately along with the average curve. Study of these shows their range in position and shape. It will be noted that certain of the curves are comparatively broad, others narrow. A rather common difference is in the relative value in the green, *i. e.*, at ·52 μ. Many of the curves would be alike except for their flatness or prominence at this point. These latter differences can probably be ascribed to differences in the pigmentation of the fovea. There is besides a considerable range in position, although the maxima of all curves lie very nearly together, namely at ·55 μ.

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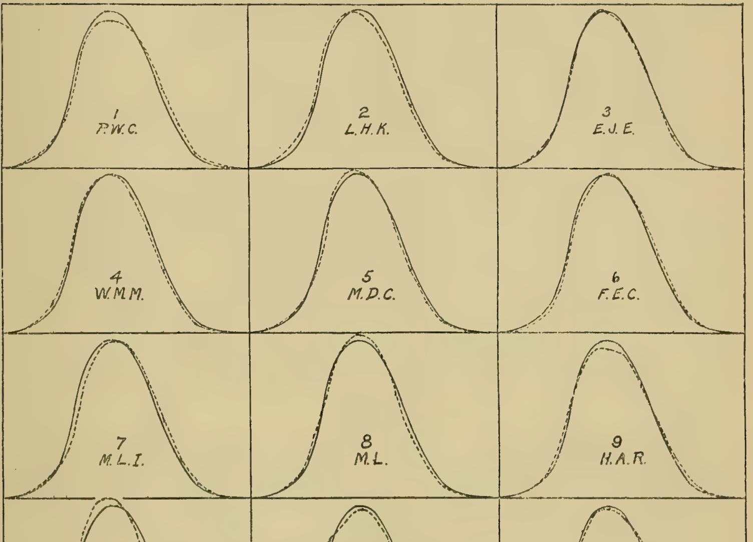
[*] Data for High Illumination as reduced by Nutting, Bull. Bur. of Stds. vol. vii. no. 2, p. 235.

[†] *Annalen der Physik,* vol. xxxiii. p. 1154 (1910).

Fig. 3.



Luminosity curves of all observers compared with the average curve.

Discussion.

Use of Luminosity Curve.—To the standard conditions of heterochromatic photometry which have been outlined above must now be added the use of the average eye as defined by the data of Table II. Upon inspection of the curves of fig. 3, it is clear that the individual variations are of such magnitude as to prevent the use of more than a very few eyes for coloured light photometry where any marked colour difference exists. The extreme observers, for instance, would measure a red light against a "white" light with a difference of 100 per cent. These differences become very much less when the light sources under comparison are any of the ordinary illuminants, but some means of obviating them is necessary in order to reach a complete solution of the photometric problem. An approximation to the condition of using a normal eye can of course always be reached by securing the cooperation of a large number of observers, and until each standardizing laboratory is prepared to obtain luminosity curves of its observers and correct their photometric work accordingly, this is the procedure to be recommended.

The most rational manner of approximating to the average eye is, however, by ascertaining the luminosity curve of each observer in the laboratory and calculating the correction to be applied to his results for the energy distribution under measurement. According to the results of this investigation, the total light is accurately the sum of the parts as measured under the standard photometric conditions. It should therefore be possible to apply known energy distributions to the observers' luminosity curves for certain physical conditions of relative intensity (such, for instance, as equality at $\cdot 58\,\mu$), and then from the relative areas of standard and test-lamp luminosity curves in the case of the observers' eyes and in the case of the average eye to obtain the correction which would bring the observers' results to average.

This mode of correction was accordingly tested. A "4 watt" carbon lamp was measured on the spectrophotometer, and by the above method its visible energy distribution was found to correspond to that of a black body at 2080° abs. The normal equal-energy spectral luminosity curves of the two observers which varied most from the normal (14 toward red, 10 toward blue) were then multiplied at each wave-length by the energy values for the 4 watt lamp (BB at 2080°), and for the tungsten lamp at 1·15 w.p.c. (BB at 2360°), the latter values being taken arbitrarily as unity at $\cdot 58\,\mu$. The areas of the four curves, measured by a planimeter, indicated that observer 10 should measure the tungsten lamp against the carbon as 3·3 per cent. higher than observer 14. An actual test, where the two lamps were measured against a comparison lamp of intermediate colour, gave a difference of 2·8 per cent. By this method of correction, therefore, a difference of nearly 3 per cent. in the readings of the two observers is reduced to ½ per cent. As these differences are of the order of magnitude of the errors with the planimeter and photometric methods, the test is taken to show the validity and feasibility of such a method of correction.

A possible and very attractive means of incorporating the average eye into photometric measurement is the development of some sensitive radiometer to supplant the eye. Such an instrument so screened as to respond at the different wave-lengths in accordance with the data of Table II. would, if sufficiently sensitive, offer the most acceptable solution to the problem. Perhaps the photoelectric cell will do this.

Summary.

This paper brings to a close the investigation on coloured light photometry as previously laid out. The practical result of the study has been to arrive at a choice of instrument and of conditions best suited to this kind of photometry, and to establish the characteristics of the average eye by which such measurements are to be carried out. By confining the actual comparison of differently coloured lights to the standardizing laboratory, so that all practical photometry is that of lights of the same colour, a solution of the problem is offered through the use of the results of this investigation. The results of the photometric method here advocated hold for the average eye under the most important illumination conditions. It is inevitable that correction factors will need to be applied to these values whenever the effective illuminations are widely different from that here adopted as standard. But such corrections will apply to the less frequent and less important conditions, that is, to ones where the loss in accuracy involved by the use of more or less rough corrections is of least importance.

Physical Laboratory,
National Electric Lamp Association,
Cleveland, Ohio.
August 1912.

XCII. *Remarks concerning Fourier's Theorem as applied to Physical Problems.* *By* Lord RAYLEIGH, *O.M., F.R.S.**

FOURIER'S theorem is of great importance in mathematical physics, but difficulties sometimes arise in practical applications which seem to have their origin in the aim at too great a precision. For example, in a series of observations extending over time we may be interested in what occurs during seconds or years, but we are not concerned with and have no materials for a remote antiquity or a distant future; and yet these remote times determine whether or not a period precisely defined shall be present. On the other hand, there may be no clearly marked limits of time indicated by the circumstances of the case, such as would suggest the other form of Fourier's theorem where everything is ultimately periodic. Neither of the usual forms of the theorem is exactly suitable. Some method of taking off the edge, as it were, appears to be called for.

The considerations which follow, arising out of a physical problem, have cleared up my own ideas, and they may perhaps be useful to other physicists.

A train of waves of length λ, represented by

$$\psi = e^{2\pi i(ct+\xi)/\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

advances with velocity c in the negative direction. If the medium is absolutely uniform, it is propagated without disturbance; but if the medium is subject to small variations, a reflexion in general ensues as the waves pass any place x. Such reflexion reacts upon the original waves; but if we suppose the variations of the medium to be extremely small, we may neglect the reaction and calculate the aggregate reflexion as if the primary waves were undisturbed. The partial reflexion which takes place at x is represented by

$$d\psi = e^{2\pi i(ct-\xi)/\lambda}\,\phi(x)dx\,.\,e^{4\pi ix//\lambda}, \quad . \quad . \quad . \quad (2)$$

in which the first factor expresses total reflexion supposed to originate at $x=0$, $\phi(x)dx$ expresses the actual reflecting power at x, and the last factor gives the alteration of phase incurred in traversing the distance $2x$. The aggregate reflexion follows on integration with respect to x; with omission of the first factor it may be taken to be

$$\mathrm{C}+i\,\mathrm{S}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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* Communicated by the Author.

where

$$C=\int_{-\infty}^{+\infty}\phi(v)\cos uv\,dv,\quad S=\int_{-\infty}^{+\infty}\phi(v)\sin uv\,dv,\ .\quad (4)$$

with $u=4\pi/\lambda$. When ϕ is given, the reflexion is thus determined by (3). It is, of course, a function of λ or u.

In the converse problem we regard (3)—the reflexion—as given for all values of u and we seek thence to determine the form of ϕ as a function of x. By Fourier's theorem we have at once

$$\phi(x)=\frac{1}{\pi}\int_{0}^{\infty}du\{C\cos ux+S\sin ux\}.\quad .\quad .\quad (5)$$

It will be seen that we require to know C and S separately. A knowledge of the *intensity* merely, viz. C^2+S^2, does not suffice.

Although the general theory, above sketched, is simple enough, questions arise as soon as we try to introduce the approximations necessary in practice. For example, in the optical application we could find by observation the values of C and S for a finite range only of u, limited indeed in eye observations to less than an octave. If we limit the integration in (5) to correspond with actual knowledge of C and S, the integral may not go far towards determining ϕ. It may happen, however, that we have some independent knowledge of the form of ϕ. For example, we may know that the medium is composed of strata each uniform in itself, so that within each ϕ vanishes. Further, we may know that there are only two kinds of strata, occurring alternately. The value of $\int\phi\,dx$ at each transition is then numerically the same but affected with signs alternately opposite. This is the case of chlorate of potash crystals in which occur repeated twinnings*. Information of this kind may supplement the deficiency of (5) taken by itself. If it be for high values only of u that C and S are not known, the curve for ϕ first obtained may be subjected to any alteration which leaves $\int\phi\,dx$, taken over any small range, undisturbed, a consideration which assists materially where ϕ is known to be discontinuous.

If observation indicates a large C or S for any particular value of u, we infer of course from (5) a correspondingly important periodic term in ϕ. If the large value of C or S is limited to a very small range of u, the periodicity of ϕ

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* Phil. Mag. vol. xxvi. p. 256 (1888); Scientific Papers, vol. iii. p. 204.

extends to a large range of x; otherwise the interference of components with somewhat different values of u may limit the periodicity to a comparatively small range. Conversely, a prolonged periodicity is associated with an approach to discontinuity in the values of C or S.

The complete curve representing $\phi(x)$ will in general include features of various lengths reckoned along x, and a feature of any particular length is associated with values of u grouped round a corresponding centre. For some purposes we may wish to *smooth* the curve by eliminating small features. One way of effecting this is to substitute everywhere for $\phi(x)$ the mean of the values of $\phi(x)$ in the neighbourhood of x, viz.

$$\frac{1}{2a}\int_{x-a}^{x+a}\phi(x)\,dx, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the range $(2a)$ of integration being chosen suitably. With use of (5) we find for (6)

$$\frac{1}{2a}\int_{x-a}^{x+a}\phi(x)dx=\frac{1}{\pi}\int_0^\infty du\frac{\sin ua}{ua}\{\mathrm{C}\cos ux+\mathrm{S}\sin ux\}, \quad (7)$$

differing from the right-hand member of (5) merely by the introduction of the factor $\sin ua \div ua$. The effect of this factor under the integral sign is to diminish the importance of values of u which exceed π/a and gradually to annul the influence of still larger values. If we are content to speak very roughly, we may say that the process of averaging on the left is equivalent to the omission in Fourier's integral of the values of u which exceed $\pi/2a$.

We may imagine the process of averaging to be repeated once or more times upon (6). At each step a new factor $\sin ua \div ua$ is introduced under the integral sign. After a number of such operations the integral becomes practically independent of all values of u for which ua is not small.

In (6) the average is taken in the simplest way with respect to x, so that every part of the range $2a$ contributes equally (fig. 1). Other and perhaps better methods of smoothing may be proposed in which a preponderance is given to the central parts. For example we may take (fig. 2)

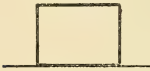
FIG. 1.

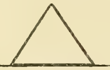
FIG. 2.

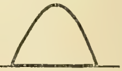
FIG 3.

$$\frac{1}{a^2}\int_0^a(a-\xi)\{\phi(x+\xi)+\phi(x-\xi)\}d\xi. \quad . \quad . \quad (8)$$

From (5) we find that (8) is equivalent to

$$\frac{2}{\pi}\int_0^\infty du\,\frac{1-\cos ua}{u^2a^2}\{\mathrm{C}\cos ux+\mathrm{S}\sin ux\}, \quad . \quad . \quad (9)$$

reducing to (5) again when a is made infinitely small. In comparison with (7) the higher values of ua are eliminated more rapidly. Other kinds of averaging over a finite range may be proposed. On the same lines as above the formula next in order is (fig. 3)

$$\frac{3}{4a}\int_{-a}^{+a}\left(1-\frac{\xi^2}{a^2}\right)\phi(x+\xi)\,d\xi$$

$$=\frac{1}{\pi}\int_0^\infty du\,\frac{\sin au-au\cos au}{\frac{1}{3}a^3u^3}\{\mathrm{C}\cos ux+\mathrm{S}\sin ux\}dx. \quad (10)$$

In the above processes for smoothing the curve representing $\phi(x)$, ordinates which lie at distances exceeding a from the point under consideration are without influence. This may or may not be an advantage. A formula in which the integration extends to infinity is

$$\frac{1}{a\sqrt{\pi}}\int_{-\infty}^{+\infty}\phi(x+\xi)e^{-\xi^2/a^2}d\xi$$

$$=\frac{1}{\pi}\int_0^\infty du\,e^{-u^2a^2/4}\{\mathrm{C}\cos ux+\mathrm{S}\sin ux\}. \quad . \quad . \quad (11)$$

In this case the values of ua which exceed 2 make contributions to the integral whose importance very rapidly diminishes.

The intention of the operation of smoothing is to remove from the curve features whose length is small. For some purposes we may desire on the contrary to eliminate features of *great* length, as for example in considering the record of an instrument whose zero is liable to slow variation from some extraneous cause. In this case (to take the simplest formula) we may subtract from $\phi(x)$—the uncorrected record—the average over a length b relatively large, so obtaining

$$\phi(x)-\frac{1}{2b}\int_{x-b}^{x+b}\phi(x)\,dx$$

$$=\frac{1}{\pi}\int_0^\infty du\left\{1-\frac{\sin ub}{ub}\right\}\left\{\mathrm{C}\cos ux+\mathrm{S}\sin ux\right\}. \quad (12)$$

Here, if ub is much less than π, the corresponding part of the range of integration is approximately cancelled and features of great length are eliminated.

There are cases where this operation and that of smoothing may be combined advantageously. Thus if we take

$$\frac{1}{2a}\int_{x-a}^{x+a}\phi(x)\,dx-\frac{1}{2b}\int_{x-b}^{x+b}\phi(x)\,dx$$

$$=\frac{1}{\pi}\int_0^\infty du\left\{\frac{\sin ua}{ua}-\frac{\sin ub}{ub}\right\}\left\{\mathrm{C}\cos ux+\mathrm{S}\sin ux\right\}, \quad (13)$$

we eliminate at the same time the features whose length is small compared with a and those whose length is large compared with b. The same method may be applied to the other formulæ (9), (10), (11).

A related question is one proposed by Stokes [*], to which it would be interesting to have had Stokes' own answer. What is in common and what is the difference between C and S in the two cases (i.) where $\phi(x)$ fluctuates between $-\infty$ and $+\infty$ and (ii.) where the fluctuations are nearly the same as in (i.) between finite limits $\pm a$ but outside those limits tend to zero? When x is numerically great, $\cos ux$ and $\sin ux$ fluctuate rapidly with u; and inspection of (5) shows that $\phi(x)$ is then small, unless C or S are themselves rapidly variable as functions of u. Case (i.) therefore involves an approach to discontinuity in the forms of C or S. If we eliminate these discontinuities, or rapid variations, by a smoothing process, we shall annul $\phi(x)$ at great distances and at the same time retain the former values near the origin. The smoothing may be effected (as before) by taking

$$\frac{1}{2a}\int_{u-a}^{u+a}\mathrm{C}\,du, \qquad \frac{1}{2a}\int_{u-a}^{u+a}\mathrm{S}\,du$$

in place of C and S simply. C then becomes

$$\int_{-\infty}^{+\infty}dv\,\phi(v)\cos uv\,\frac{\sin av}{av},$$

$\phi(v)$ being replaced by $\phi(v)\sin av\div av$. The effect of the added factor disappears when av is small, but when av is large, it tends to annul the corresponding part of the integral. The new form for $\phi(x)$ is thus the same as the old one near the origin but tends to vanish at great distances on either side. Case (ii.) is thus deducible from case (i.) by the application of a smoothing process to C and S, whereby fluctuations of small length are removed.

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[*] Smith's Prize Examination, Feb. 1, 1882; Math. and Phys. Papers, vol. v. p. 367.

We may sum up by saying that a smoothing of $\phi(x)$ annuls C and S for large values of u, while a smoothing of C and S (as functions of u) annuls $\phi(x)$ for values of x which are numerically great.

Terling Place, Witham,
October 1912.

XCIII. *On the Gas-equation.*

By S. D. Wicksell, *Lund*, *Sweden* [*].

In the famous gas-equation of van der Waals:

$$\left(\mathrm{P}+\frac{a}{v^2}\right)(v-b)=\mathrm{R}\theta, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

a and b are small constants depending, a on the mutual attraction of the molecules, and b on the volume of the molecules.

P is the pressure of the gas, v its volume, and θ denotes the absolute temperature. R is the gas-constant.

In reality, however, the quantities a and b are not constant. They vary both with temperature and pressure.

In the following I will regard a and b as functions of the temperature only; thus getting a gas-equation that covers the case of Clausius and several others.

It is the object of this paper to transform the gas-equation into a more convenient form by means of series, and to study the quantities a and b, expressing them in known and measurable quantities.

The equation (1) can be transformed into

$$\mathrm{P}v\left(1-\frac{b}{v}\right)=\mathrm{R}\theta\left[1-\frac{a}{v\mathrm{R}\theta}\left(1-\frac{b}{v}\right)\right].$$

We express P in atmospheres;

v in the volume of one gram-molecule of the ideal gas at one atmosphere and 0° centigrade;

θ in degrees centigrade.

By index zero I mean the value at 0° C.

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[*] Communicated by the Author.

We then have

$$R=\frac{1}{\theta_0},$$

and putting

$$a\frac{\theta_0}{\theta}=\alpha,$$

$$1/v=x,$$

$$P\cdot\frac{\theta_0}{\theta}=y,$$

we get

$$y(1-bx)=x-\alpha x^2+\alpha bx^3. \quad . \quad . \quad . \quad . \quad (2)$$

I now want x expressed as a series in powers of y or, which is the same, in powers of P.

The first question is how and when this series is convergent.

The equation (2) gives

$$x=F(y),$$

and the series is convergent for all values of y less than the absolute value of the least y that gives $F(y)$ a singularity.

It is easily seen that $F(y)$ can have no other finite singularity than when it ramifies, and that occurs when y has such a value that the cubic (2) has equal roots. For every value of the parameters α and b, that is of the temperature, there are three such values of y, always one negative and two positive or imaginary. They are given by the equation

$$4b^4y^3+y^2(12b^3+8\alpha b^2)-y(20\alpha b-12b^2-4\alpha^2)+4b-\alpha=0.$$

It is seen from this equation that when $\alpha=4b$ or $\theta=\frac{a}{4b}\theta_0$ one of the roots is equal to zero. The least absolute value of the roots of the equation is the interval of convergence. For $\theta=\frac{a}{4b}\theta_0$ this interval must be equal to zero. It is also easy to see that when θ grows the equation has two positive roots and one negative, which always grow until $\theta=\frac{8a}{27b}\theta_0$, when the positive roots coincide and then turn imaginary. At $\theta=\frac{8a}{27b}\theta_0$ the interval of convergence is $|y|=\frac{1}{8b}$. $\theta=\frac{8a}{27b}\theta_0$ is, theoretically from van der Waals's equation, the critical temperature. At $\theta=\infty$ the interval of convergence will be $|y|=\frac{1}{b}$.

The series in powers of P has an interval of convergence

$$P_c=\frac{a}{27b^2}\delta,$$

where $\delta=0$ for $\theta=\frac{a}{4b}\theta_0$; and then grows with θ and becomes equal to 1 for $\theta=\frac{8a}{27b}\theta_0$; thereafter δ grows infinitely with θ.

It will be seen from numerical examples that the series generally converges very fast.

In order to find the series we put

$$x=a_1y+a_2y^2+a_3y^3+\ \ldots .$$

and substitute this in the equation (2).

We then get

$$\begin{aligned} y= & \,a_1y+a_2y^2+a_3y^3+a_4y^4+a_5y^5+\ \ldots . . \\ & +b(a_1y^2+a_2y^3+a_3y^4+a_4y^5+\ \ldots . .) \\ & -\alpha[a_1^2y^2+2a_1a_2y^3+(a_2^2+2a_1a_3)y^4+(2a_1a_4+2a_2a_3)y^5+\ldots] \\ & +b\alpha[a_1^3y^3+3a_1^2a_2y^4+3(a_1^2a_3+a_2^2a_1)y^5+\ \ldots .]. \end{aligned}$$

As α and b are supposed independent of P, or which is the same, of y, we can put the coefficients of the powers of y equal to zero.

That gives us

$$\begin{aligned} & a_1=1, \\ & a_2=\alpha-b, \\ & a_3=2\alpha a_2-ba_2-b\alpha, \\ & a_4=\alpha(a_2+2a_3)-ba_3-3b\alpha a_2, \\ & a_5=2\alpha(a_4+a_2a_3)-ba_4-3b\alpha(a_3+a_2^2). \end{aligned}$$

Putting $\alpha-b=\phi$ and solving the system we get

$$\begin{aligned} & a_1=1, \\ & a_2=\phi, \\ & a_3=2\phi^2-b^2, \\ & a_4=5\phi^3-5b^2\phi-b^3, \\ & a_5=14\phi^4-21\phi^2b^2-6b^3\phi+2b^4. \end{aligned}$$

And finally we get

$$x=y[1+\phi y+(2\phi^2-b^2)y^2+(5\phi^3-5b^2\phi-b^3)y^3 \\ +(14\phi^4-21\phi^2b^2-6b^3\phi+2b^4)y^4+\ldots]. \quad (3)$$

For the ideal gas we have

$$y=x,$$

and we see that the series $1+\phi y+\ldots$ can, according to the nature of the constants, have no value equal to zero. Accordingly, we have a right to invert the series, and thus we get

$$\mathrm{P}v=\frac{\theta}{\theta_0}\left[1-\frac{\theta_0}{\theta}\phi\mathrm{P}-\left(\frac{\theta_0}{\theta}\right)^2(\phi^2-b^2)\mathrm{P}^2-\left(\frac{\theta_0}{\theta}\right)^3(2\phi^3-3\phi b^2-b^3)\mathrm{P}^3 \right. \\ \left. -\left(\frac{\theta_0}{\theta}\right)^4(5\phi^4-10\phi^2b^2-4\phi b^3+b^4)\mathrm{P}^4-\ldots\right] \quad . \quad (4)$$

The following numerical examples will illustrate the magnitude of the different terms.

For carbon-dioxide we take at 0° C.,

$$a=0{\cdot}011$$
$$b=0{\cdot}003.$$

(All values are, when nothing else is stated, taken from the work *Die Zustandsgleichung* by Prof. Dr. Kuenen.)

Then (4) becomes

$$\mathrm{P}v=1-0{\cdot}008\mathrm{P}-0{\cdot}00005\mathrm{P}^2-0{\cdot}000003\mathrm{P}^3.$$

For ethylene we take at 20° C.

$$a=0{\cdot}00786$$
$$b=0{\cdot}0024,$$

and get

$$\mathrm{P}v=1{\cdot}073-0{\cdot}0050\,\mathrm{P}-0{\cdot}000017\,p^2-0{\cdot}00000011\,\mathrm{P}^3.$$

The results are given by the following table :—

P.	P 0·0050.	P^2 0·000017.	P^3 0·00000011.	P*v*.	P*v*. from (1).
31·9	0·16	0·02	0·003	0·89	0·89
45·8	0·22	0·04	0·01	0·80	0·78

It is seen that at 30 atmospheres we need not go farther than to the second power of P in order to obtain a value of P*v* with two decimals. It is furthermore seen that for relatively low pressures, generally as high as 5 atm., the second power of P can be neglected, if we want P*v* given with three decimals.

We then have

$$\mathrm{P}v = \frac{\theta}{\theta_0} - \phi \mathrm{P}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or

$$\mathrm{P}v - \mathrm{R}\theta = \phi \mathrm{P}.$$

That is, the deviation from the ideal gas-equation is proportional to the pressure. This relation can be written

$$\frac{\mathrm{P}' v' - \mathrm{R}\theta}{\mathrm{P}'' v'' - \mathrm{R}\theta} = \frac{\mathrm{P}'}{\mathrm{P}''}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where P′ and v' are referred to one case and P″ and v'' to another at the same temperature.

The equation (6) includes no quantity characteristic for the gas, and therefore can be regarded as a general gas-law in the second approximation if Boyle-Mariotte-Gay Lussac's law is regarded as the first approximation.

It will be of some interest to see what form the expression of the expansion coefficient k^{P} will take as a series in powers of P and θ.

We have

$$\frac{dv}{v_0} = k^{\mathrm{P}} d\theta,$$

and get from (4)

$$\mathrm{P}dv = \frac{d\theta}{\theta_0}\left[1 + \mathrm{P}(\phi + b)\frac{\theta_0}{\theta} + \mathrm{P}^2(3\phi^2 + 2\phi b - b^2)\left(\frac{\theta_0}{\theta}\right)^2 \right.$$
$$\left. + \mathrm{P}^3(10\phi^3 - 9\phi b^2 + 6\phi^2 b - 4b^3) + \ldots . \right].$$

From (3) we get

$$\frac{1}{\mathrm{P}v_0} = 1 + \mathrm{P}\phi_0 + \mathrm{P}^2(2\phi_0^2 - b^2) + \mathrm{P}^3(5\phi_0^3 - 5\phi_0 b^2 - b^3) + \ldots$$

As

$$\phi_0 = a - b,$$

we finally get

$$k^{\mathrm{P}} = \frac{1}{\theta_0}\left[1 + \mathrm{P}\left(\frac{\theta_0^2 + \theta^2}{\theta^2} a - b\right) + \mathrm{P}^2\left(\frac{3\theta_0^4 + \theta_0^2\theta^2 + 2\theta^4}{\theta^4} a \right.\right.$$
$$\left.\left. - \frac{4\theta_0^3 + \theta_0^2\theta + 4\theta^3}{\theta^3} ab + b^2\right) \ldots \right],$$

or if

$$\mathrm{P}\frac{\theta_0}{\theta} = y, \quad a\frac{1}{\theta\theta_0} = \beta, \quad \frac{b}{\theta_0} = \gamma,$$

$$k^{\mathrm{P}} = 1/\theta_0[1 + y\{(\theta_0^2 + \theta^2)\beta - \theta\gamma\} + y^2\{(3\theta_0^4 + \theta_0^2\theta^2 + 2\theta^4)\beta^2$$
$$- (4\theta_0^3 + \theta_0^2\theta + 4\theta^3)\beta\gamma + \gamma^2\theta^2\} + \ldots].$$

The convergence of this series I have not ascertained otherwise than numerically. It is clear, however, that the series cannot converge for a value of P or y greater than the interval of convergence of (3) when $\theta=\theta_0$.

For not too high pressures we can as before neglect all but the first power in P and get

$$k^{\mathrm{P}}=1/\theta_0\left[1+\mathrm{P}\left(\frac{\theta_0{}^2+\theta^2}{\theta^2}a-b\right)\right]. \quad . \quad . \quad . \quad (7)$$

That is, if a and b do not vary with P we have by unvarying temperature:

$$\mathrm{A}=\frac{k_\theta^{\mathrm{P}_1}\theta_0-1}{k_\theta^{\mathrm{P}_2}\theta_0-1}=\frac{\mathrm{P}_1}{\mathrm{P}_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k_θ^{P} is the expansion-coefficient at constant pressure by a temperature equal to θ and a pressure equal to P.

This formula is similar to (6).

I have tested this formula numerically, and the results are given by the following table.

I have used values of k given in the tables of Landolt-Börnstein. Those values are not, however, referred to a constant temperature. They denote the mean expansion for an *interval* of temperature :—

For Carbon dioxide.

I.

Temp.-interval (0° – 20° C.). Pressure about 1–2 atm.

	k.	P.		A.	$\frac{\mathrm{P}_1}{\mathrm{P}_2}$.
(Case 1)	0·0037128	518 mm. Hg.	$\frac{\text{case 1}}{\text{case 2}}$	0·517	0·519
(„ 2)	37602	998	$\frac{\text{case 2}}{\text{case 3}}$	0·376	0·376
(„ 3)	37972	1377	$\frac{\text{case 1}}{\text{case 3}}$	0·727	0·725

II.

Temp.-interval (64° – 100°). Pressure about 17–40 atm.

	k.	P.		A.	$\frac{\mathrm{P}_1}{\mathrm{P}_2}$.
(Case 1)	0·004747	12988 mm. Hg.	$\frac{\text{case 1}}{\text{case 2}}$	0·61	0·68
(„ 2)	5435	18856	$\frac{\text{case 2}}{\text{case 3}}$	0·37	0·49
(„ 3)	6574	26212	$\frac{\text{case 1}}{\text{case 3}}$	0·60	0·71

In this case the pressure is too high to allow us to neglect the second power of P.

For Air.

III.

Temp.-interval unknown. Pressure 1–4 atm.

	k.	P.		A.	$\frac{P_1}{P_2}$.
(Case 1)	0·0036706	700 mm. Hg.	$\frac{\text{case 1}}{\text{case 2}}$	0·27	0·30
(„ 2)	36944	2525	$\frac{\text{case 2}}{\text{case 3}}$	0·25	0·29
(„ 3)	36964	2620	$\frac{\text{case 1}}{\text{case 3}}$	0·95	0·96

In cases I. and III. the convergence of (8) is evident.

From equations (5) and (7) we evidently can determine a and b in terms of known and measurable quantities.

We have :—

$$\frac{\theta}{\theta_0}-\mathrm{P}v=\mathrm{P}\left(a\frac{\theta_0}{\theta}-b\right),$$

$$k^{\mathrm{P}}-1 \ =\mathrm{P}\left(a\frac{\theta_0^2+\theta^2}{\theta^2}-b\right);$$

and we get

$$\left.\begin{aligned} a&=\frac{k^{\mathrm{P}}\theta_0-1-\left(\frac{\theta}{\theta_0}-\mathrm{P}v\right)}{(\theta_0^2-\theta_0\theta+\theta^2)\,.\,\mathrm{P}}\theta^2,\\ b&=\frac{\theta_0\theta\,(k^{\mathrm{P}}\theta_0-1)-\left(\frac{\theta}{\theta_0}-\mathrm{P}v\right)(\theta_0^2+\theta^2)}{(\theta_0^2--\theta_0\theta+\theta^2)\,.\,\mathrm{P}}\end{aligned}\right\} \quad . \quad . \quad (9)$$

According to van der Waals those expressions ought not to vary. If we regard a and b as constant we can take the case of 0° C. when $\theta=\theta_0$, and get

$$\left.\begin{aligned} a&=k_0^{\mathrm{P}}\theta_0-1- \ (1-v_0')\\ b&=k_0^{\mathrm{P}}\theta_0-1-2(1-v_0')\end{aligned}\right\}; \quad . \quad . \quad . \quad (10)$$

where v_0' is the volume of one gram-molecule of the gas at $\theta°$ and 1 atmosphere, and a and b consequently referred to one gram-molecule of gas.

From (10) we get

$$a-b=1-v_0'.$$

That $a-b$ should be expressed in a similar way can *a priori* be regarded as probable, because the influence of a tends to diminish the volume v_0' and the influence of b to expand it.

That this expression is practically true we can see from the following example.

We choose hydrogen as the ideal gas and get the normal volume $v_1=22{\cdot}4452$ litres, which is a little too great. The volume of one gram-molecule of carbon dioxide at 0° C. and 1 atmosphere is $v_2=22{\cdot}2635$ litres.

$$v_0' \text{ for carbon dioxide is equal to } \frac{v_2}{v_1}.$$

$$\text{Consequently} \qquad 1-v_0'=0{\cdot}0081,$$

$$a=0{\cdot}0134, \quad b=0{\cdot}0054, \quad a-b=0{\cdot}0080.$$

From the equation (9) it ought to be possible by trial to determine how a and b vary with temperature at constant pressure, at least when that pressure is not too high, because all the terms in the formula are measurable quantities.

From these lines it is furthermore seen that a series of the form (4) is identically the same as an equation of the form (1), a and b being any function of the temperature. It is evident that from a series in powers of P it ought to be easy to determine by trial what kind of functions of the temperature the coefficients are, thus getting the variation of a and b by aid of equation (4) for even higher pressures, at least inasmuch as the form of van der Waals' equation is true.

Furthermore, a series of the form (4) is more convenient to use by determining the volume than the solution of the cubic (1).

XCIV. *The Effect of the Transition Layer of a Liquid on its Surface Tension.* By R. D. KLEEMAN, *D.Sc., B.A.*[*]

IT requires the expenditure of energy to produce an increase in the area of surface of a liquid. The surface-tension is therefore the work done, keeping the temperature constant, in producing unit increase in the area of surface of the liquid. Now this increase of surface may be produced in a variety of ways, since it follows from thermodynamics that the work done during an isothermal process between given limits is independent of the nature of the path of the process. One way suggested by Laplace is to suppose a slab of liquid cut into two parts by an imaginary plane, and the parts then separated by an infinite distance from one another. If W denote the total amount of work done during the process of separation, and A the amount of new surface formed, the surface-tension λ_2 is given by

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[*] Communicated by the Author.

$$\lambda_2 = \frac{W}{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the distribution of the molecules in the new surfaces formed is the same as in the interior of the liquid, and the law of molecular attraction were known, the work done could at once be calculated. But the distribution of the molecules in the surface of a liquid is not the same as in the interior, a transition layer is formed in which the density changes continuously from that of the liquid on one side of the layer to that of the vapour on the other side.

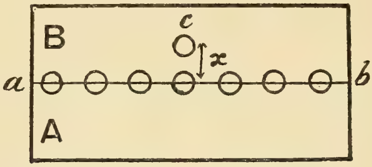
The nature of the effect of the formation of a transition layer on the surface tension can be easily investigated. Suppose that on separation of the two slabs of liquid in the foregoing process, no change takes place in the distribution of the molecules in the surfaces of the slabs. The work done, as before, is W. Now suppose the transition layers to be formed. This will require that the surface layer of the liquid undergoes expansion in different degrees in different parts. Since the complete process of increase of the surface of a liquid is a reversible one, we must suppose that the formation of the transition layer takes place in such a way that external work is done during the process, and that it is a reversible one. We may, for example, suppose that the liquid is contained in a cylinder in which the piston is in contact with the liquid surface in question exerting a pressure tending to prevent the formation of the layer. This work is done at the expense of the heat supplied since the temperature has to be kept constant during the process. Let w denote the amount of work in this case. The actual surface-tension of a liquid is then given by

$$\lambda_1 = \frac{W - w}{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Thus we see that the production of a transition layer on the surface of a liquid has the effect of decreasing the magnitude of the surface tension.

A formula will be developed in this paper which expresses W in terms of quantities which can be measured. Since λ_1 can also be measured, the value of w can be calculated by means of equation (2).

Let a mass of liquid represented by AB in the figure be cut into two slabs by an imaginary plane *ab*. Let the attraction of the slab A on a molecule *c* at a distance *x* from the plane *ab* be denoted by F_x. The amount of surface tension λ_x contributed by the molecule on separation of the slabs, supposing no transition layer formed, is given by



$$2\lambda_x = \int_{\infty}^{x} F_x \,.\, dx.$$

Since the attraction between two molecules decreases with their distance of separation

$$\left[\int F_x \,.\, dx\right]_{x=\infty} = 0,$$

and hence

$$2\lambda_x = \int F_x \,.\, dx, \quad \text{or } 2\frac{d\lambda_x}{dx} = F_x.$$

The amount of intrinsic pressure P_x contributed by the molecule is equal to F , and hence the foregoing equation may also be written

$$2\frac{d\lambda_x}{dx} = P_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In order to be able to deal with all the molecules in the slab B in this manner, and to compare the results with one another, it is necessary to know the relative distribution of the mean positions of the molecules in a liquid. In a previous paper * it was shown that we may suppose that the molecules in a pure liquid are situated at the points of intersection of three systems of parallel equidistant planes which intersect each other at right angles. Let us suppose that one of the planes coincides with the plane *ab*. Let us take one of the molecules in *ab* as zero of coordinates. Consider the molecules lying on a line at right angles to *ab* and passing through the zero. We then have similarly as before

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* Phil. Mag. April 1911, pp. 537–538.

$$2\left\{\frac{d\lambda_x}{dx}+\frac{d\lambda_{2x}}{d(2x)}+\frac{d\lambda_{3x}}{d(3x)}+\ldots\right\}=2\left\{\frac{d\lambda_x}{dx}+\frac{1}{2}\frac{d\lambda_{2x}}{dx}+\frac{1}{3}\frac{d\lambda_{3x}}{dx}+\ldots\right\}$$
$$=\left(\mathrm{F}_x+\mathrm{F}_{2x}+\mathrm{F}_{3x}+\ldots\right) \quad \ldots\ldots \quad (4)$$

where x denotes the distance of separation of the molecules in the liquid. The intrinsic pressure P_n of the liquid is given by

$$\mathrm{P}_n=\frac{1}{x^2}(\mathrm{F}_x+\mathrm{F}_{2x}+\mathrm{F}_{3x}+\ldots), \quad \ldots\ldots \quad (5)$$

and the surface-tension λ_2, on the supposition that no transition layer is formed, is given by

$$\lambda_2=\frac{1}{x^2}(\lambda_x+\lambda_{2x}+\lambda_{3x}+\ldots), \quad \ldots\ldots \quad (6)$$

where the factor $\frac{1}{x^2}$ denotes the number of rows of molecules standing on one cm.^{2}.

If the law of molecular attraction were exactly known we could express the quantities $\lambda_x, \lambda_{2x}, \ldots.$, in terms of the attraction constant of the molecules, that is, we could deduce a number of relations of the form

$$\lambda_{nx}=\psi_1(nx, k), \quad \ldots\ldots \quad (7)$$

where k denotes the molecular attraction constant. On substituting for λ_{nx} in equations (4) and (6) from the above equation, we obtain two equations from which k may be eliminated. The resultant equation and equation (5) give an equation containing P_n, λ_2, and x, only. The form of this equation depends on the form of the function $\psi_1(nx, k)$. A form of the equation which very approximately represents the facts is obtained from the following considerations.

Let us suppose that the attraction between two molecules is given by an expression of the form $\frac{k}{z^m}$, where z denotes the distance of separation of the molecules, and k and m are constants. From equation (7) we then have

$$\lambda_{nx}=\lambda_x c_n \quad \ldots\ldots \quad (8),$$

where c_n is a function of n and m. Equations (4), (5), and

(6) then give

$$\left\{\frac{1+\frac{c_2}{2}+\frac{c_3}{3}+\ldots}{1+c_2+c_3+\ldots}\right\}\frac{2}{x_2}\left\{\frac{d(\lambda_2 x^2)}{dx}\right\}_{\mathrm{T}}=\frac{\mathrm{X}2}{x^2}\left\{\frac{d(\lambda_2 x^2)}{dx}\right\}_{\mathrm{T}}=\mathrm{P}_n \quad \ldots\ldots \quad (9)$$

But the attraction between two molecules is probably not given by an expression of the above form. c_n is therefore probably a function of x as well as of n and m. But it will obviously not vary very much with x, since the law of attraction could always approximately be represented by an expression of the form given. The variation of the values of c_n with x, it will be seen, affects the value of the function X very little on account of its form. It follows therefore that equation (9) very approximately represents the facts, and that the value of X can be determined with fair accuracy from a form of the law of molecular attraction which is approximately correct.

In previous papers * it was shown that the law of attraction between two molecules is approximately given by $\frac{k}{z^5}$, where z denotes their distance of separation and k a quantity which is constant at constant temperature. This law may therefore be used to calculate the value of X. The calculations will be facilitated by the following considerations. Let a_1 denote the work done against the attraction of the molecules in the plane ab on moving the molecule situated in the slab B at a distance x from the zero of coordinates to an infinite distance from the plane ab. Let a_2 denote the work done in moving the molecule situated at a distance $2x$ from the zero of coordinates to an infinite distance from the plane, and a_3 the work done on transporting the molecule at a distance $3x$, &c. The total work A_1 done on moving the molecule at a distance x to infinity against the attraction of all the molecules in the slab A is therefore given by

$$\mathrm{A}_1=(a_1+a_2+a_2+\ldots a_n).$$

The total work A_2 done on moving the molecule at a distance $2x$ to infinity against the attraction of all the molecules in the slab A is therefore given by

$$\mathrm{A}_2=(a_2+a_3+a_4+\ldots a_n)\,;$$

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* Phil. Mag. May 1910, pp. 795–807; Proc. Camb. Phil. Soc. vol. xvi. pt. 7, pp. 586–587.

and similarly

$$A_3 = (a_3 + a_4 + a_5 + \ldots a_n),$$

and so on. We then have $2\lambda_{nx} = A_n$, and from this equation, the special case $2\lambda_x = A_1$, and equation (8), we obtain

$$c_n = \frac{A_n}{A_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It is necessary next to calculate the values of

$$a_1, a_2, a_3, \ldots a_n.$$

The component of attraction at right angles to the plane *ab* of a molecule lying in the plane on a molecule in the slab B at the distance nx from the zero of coordinates is given by $\frac{k}{z^5}\,\frac{nx}{z}$, where z denotes the distance of separation of the molecules. The coordinates of the latter molecule are $(nx, 0, 0)$, and if those of the former be denoted by (nx, wx, vx) we have

$$z = \sqrt{(n^2x^2 + w^2x^2 + v^2x^2)},$$

and the above expression becomes

$$\frac{kn}{x^5\{n^2 + w^2 + v^2\}^3}.$$

The component of attraction f_{nx} exerted by all the molecules in the plane *ab* is therefore equal to

$$\frac{k}{(nx)^5} + 4\sum_{w=1}^{w=\infty}\sum_{v=1}^{v=\infty}\frac{kn}{x^5\{n^2 + w^2 + v^2\}^3} + 4\sum_{v=1}^{v=\infty}\frac{kn}{x^5(n^2 + v^2)^3}.$$

The work a_n required to move the molecule to infinity is given by

$$a_n = \int f_{nx}\,d(nx) = x\,\frac{k}{4n^4x^4} + \sum_{w=1}^{w=\infty}\sum_{v=1}^{v=\infty}\frac{k}{x^4\{n^2 + w^2 + v^2\}^2} + \sum_{v=1}^{v=\infty}\frac{k}{x^4(n^2 + v^2)^2}.$$

On developing the right-hand side of this equation into a series (we need not retain the terms involving values of v and w higher than 3), the value of a_n can readily be calculated for different values of n. The equation gives

$$a_1 = \frac{k}{x^4}\cdot 7532, \quad a_2 = \frac{k}{x^4}\cdot 15195, \quad a_3 = \frac{k}{x^4}\cdot 05056, \quad \text{and} \quad a_4 = \frac{k}{x^4}\cdot 0219.$$

It is not necessary to obtain values of a_n of a higher order than the fourth.

We have accordingly

$A_1 = \cdot9776\frac{k}{x^4}$, $A_2 = \cdot2244\frac{k}{x^4}$, $A_3 = \cdot07246\frac{k}{x^4}$, and $A_4 = \cdot0219\frac{k}{x^4}$,

and hence equation (9) by means of equation (10) becomes

$$\frac{\cdot876\times2}{x^2}\left\{\frac{d(\lambda_2 x^2)}{dx}\right\}_{T} = P_n. \quad . \quad . \quad . \quad . \qquad (11)$$

On comparing this equation—which represents the effect of all the molecules in the slab B_1 with equation (3)—which represents the effect of a single molecule, we see that the difference in form consists of the factor ·876 occurring in one equation where the factor 1 occurs in the other. Since

$$x = \left(\frac{m_a}{\rho}\right)^{1/3},$$

where ρ denotes the density of the substance and m_a the absolute mass of a molecule, equation (11) may be written

$$\frac{\cdot876\times6\rho^2}{m_a^{1/3}}\left\{\frac{d}{d\rho}\left(\frac{\lambda_2}{\rho^{2/3}}\right)\right\}_{T} = -P_n. \quad . \quad . \quad . \qquad (12)$$

The foregoing equation may be thrown into a form which is more convenient. In a previous paper * it was shown that

$$P_n = \frac{dU}{dv} = -\rho^2\frac{dU}{d\rho},$$

where U denotes the energy expended in overcoming the molecular attraction on separating the molecules of a gram of matter by an infinite distance from one another. The equation then becomes

$$\frac{\cdot876\times6}{m_a^{1/3}}\cdot d\left(\frac{\lambda_2}{\rho^{2/3}}\right) = dU. \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

Integrating it we obtain

$$\frac{\cdot876\times6\lambda}{m_a^{1/3}\rho^{2/3}} = U + C,$$

where C is an arbitrary constant. The value of the constant C may be determined from the following considerations. When the density of the substance is infinitely small, or x is infinitely great, $U=0$ and $\lambda_2=0$. The expression $\frac{\lambda}{\rho^{2/3}}$ may be written $\frac{K}{x^{8/3}}$, where K is a constant, if we assume that the

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* Proc. Camb. Phil. Soc. vol. xvi. pt. vi. pp. 543–546.

attraction between two molecules is given by $\frac{k}{z^5}$. The expression therefore becomes equal to zero when the density of the substance becomes infinitely small. This holds whether the above expression for the molecular attraction is exactly true or not. Thus suppose that the molecular attraction is given by the expression $\frac{k}{z^2}$. The expression $\frac{\lambda_2}{\rho_{2/3}}$ then becomes $\frac{K}{x^{1/3}}$, and thus as before becomes equal to zero when the density of the substance becomes infinitely small. But the molecular attraction which gives rise to surface-tension must decrease at a much greater rate with the distance of separation of the molecules than follows from the foregoing expression[*], and $\frac{\lambda_2}{\rho^{2/3}}$ must therefore be equal to zero when the density of the substance is infinitely small. On applying the equation under consideration to matter of infinitely small density we obtain $C=0$, and thus

$$\cdot 876 \times 6\lambda_2 = U m_a^{1/3} \rho^{2/3}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

U denotes the energy expended in overcoming the molecular attraction on separating the molecules of a gram of substance an infinite distance from one another, and if u denotes the sum of the internal energies of the molecules, the internal heat of evaporation L is given by

$$L = U_1 - U_2 + u_1 - u_2,$$

where the suffix 1 refers to the liquid and 2 to the saturated vapour. Let us assume that the internal energy of a molecule is independent of the vicinity of other molecules, in which case $u_1 - u_2 = 0$. If the density of the saturated vapour is small in comparison with that of the liquid, as is the case at low temperatures, $U_2 = 0$ and consequently $U_1 = L$. Thus, on the above assumption, the values of λ_2 can be calculated for low temperatures of the liquid. This has been carried out for four liquids, the results being contained in the table given, which also contains the values of λ_1 obtained by Ramsay & Shields[†]. The values of L were taken from a paper by Mills[‡]. The values of λ_2 are greater than those of λ_1, as was indicated at the beginning of the paper. The difference $(\lambda_2 - \lambda_1)$ is the external work done in the formation of the transition layer. It will be seen that it is somewhat less than λ_1, and approximately independent of the temperature over a considerable range. The effect of the transition layer on the surface-tension is thus quite large.

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[*] Phil. Mag. Jan. 1911, pp. 89–90.

[†] Phil. Trans. of the Roy. Soc., A, vol. clxxxiv. p. 647 (1893).

[‡] Journ. of Phys. Chem. vol. viii. p. 405 (1904).

Ethyl oxide, $C_4H_{10}O$.						Carbon tetrachloride, CCl_4.					
T.	L_1.	ρ.	λ_2.	λ_1.	$\lambda_2-\lambda_1$.	T.	L_1.	ρ.	λ_2.	λ_1.	$\lambda_2-\lambda_1$.
313	75·36	·6894	23·12	14·05	9·07	363	40·62	1·4554	26·18	17·60	8·58
323	73·01	·6764	22·12	12·94	9·18	373	39·68	1·4343	25·33	16·48	8·85
333	70·79	·6658	21·20	11·80	9·40	383	38·64	1·4124	24·41	15·41	9·00
343	68·35	·6532	20·27	10·72	9·55	393	37·63	1·3902	23·52	14·32	9·20
353	65·85	·6402	19·27	9·67	9·60	403	36·58	1·3680	22·62	13·27	9·35
363	63·31	·6250	18·19	8·63	9·56	413	35·56	1·3450	21·94	12·22	9·72
373	60·33	·6105	17·16	7·63	9·53	423	34·42	1·3215	20·81	11·21	9·60
Methyl formate, $C_2H_4O_2$.						Benzene, C_6H_6.					
303	107·5	·9598	38·35	23·09	15·26	353	85·62	·8415	29·87	20·28	9·59
313	103·9	·9447	36·64	21·56	15·08	363	83·74	·8041	28·97	19·16	9·81
323	99·51	·9294	34·74	20·05	14·69	373	81·98	·7927	28·06	18·02	10·04
333	95·59	·9133	32·98	18·58	14·40	383	80·05	·7809	27·15	16·86	10·29
343	92·16	·8968	31·94	17·55	13·89	393	78·12	·7692	26·24	15·71	10·53
353	88·03	·8803	29·65	15·70	13·95	403	76·10	·7568	25·28	14·57	10·71
363	85·10	·8636	28·25	14·29	13·96	413	74·09	·7440	24·33	13·45	10·88

In previous papers a formula for the surface-tension λ of a liquid was obtained on the supposition that no transition layer is formed and that the molecular attraction is given by the expression

$$\phi\left(\frac{T}{T_c}\,\frac{x_c}{z}\right)\frac{(\Sigma\sqrt{m_1'})^2}{z^5},$$

where m_1' denotes the atomic weight of an atom of a molecule. This gave

$$\lambda=k\left(\frac{\rho}{m_1}\right)^2(\Sigma\sqrt{m_1'})^2,$$

where m_1 denotes the molecular weight relative to hydrogen, and k is a quantity which has the same value for all substances at corresponding states. This equation was found to agree well with the facts. It follows, therefore, that each of the quantities λ_1, λ_2, and $(\lambda_2-\lambda_1)$ obeys the relation expressed by this equation.

The influence of the surrounding vapour of a liquid on its surface-tension may approximately be taken into account by supposing that we are dealing with a liquid of density $(\rho_1-\rho_2)$ which is not surrounded by vapour, where ρ_1

denotes the density of the liquid and ρ_2 that of the surrounding vapour. The surface-tension is thus approximately given * by

$$\lambda_1 = 32{\cdot}96(\rho_1-\rho_2)^4\left(\frac{\Sigma\sqrt{m_1'}}{m_1\rho_c}\right)^2. \quad . \quad . \quad . \quad (15)$$

At low temperatures

$$L = \frac{2073\,\rho_1^2}{m_1^{7/3}\rho_c^{2/3}}(\Sigma\sqrt{m_1'})^2 \dagger,$$

and therefore more generally

$$L = \frac{2073(\rho_1-\rho_2)^2}{m_1^{7/3}\rho_c^{2/3}}(\Sigma\sqrt{m_1'})^2.$$

Equation (14) may therefore be written

$$\lambda_2 = 203{\cdot}2(\rho_1-\rho_2)^{8/3}\frac{(\Sigma\sqrt{m_1'})^2}{m_1^2\rho_c^{2/3}}. \quad . \quad . \quad . \quad (16)$$

Equation (14) may also be applied to mixtures. If two liquids 1 and 2 are mixed in the proportion of n_1 and n_2, and no new molecules are formed in the mixture, the value of U is given by

$$U = \frac{L_1n_1+L_2n_2}{n_1+n_2}+H,$$

where H denotes the heat of solution per gram of solution, and L_1 the internal heat of evaporation of a gram of liquid 1, and L_2 that of a gram of liquid 2. The values of L_1, L_2 and H_1 can usually be obtained and hence the value of λ_2 calculated.

The relative concentration of the ingredients in the transition layer of a mixture of substances is not the same as in the interior of the mixture. This property of a mixture is known as adsorption. Its thermodynamical treatment was first given by Willard Gibbs. It follows therefore that $(\lambda_2-\lambda_1)$ represents the external work done during the formation of the transition layer, and in altering the relative proportion of its ingredients. Equation (14) is therefore very useful, since it furnishes information on the nature of the transition layer in addition to that given by Gibbs's investigation. It may therefore help to clear up the important part played by the surfaces of contact in chemical changes.

London, July 10, 1912.

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* Phil. Mag. Jan. 1911, pp. 99–101.

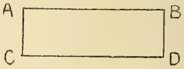
† Phil. Mag. Oct. 1910, pp. 686–687.

XCV. *A Determination of Poisson's Ratio.* *By* I. Williams, *M.Sc., Lecturer and Demonstrator in Physics in the University of Bristol*[*].

THE object of the experiments about to be described was to determine Poisson's Ratio for a steel bar from observations on the distortion of the cross-section.

Let ABCD represent either the normal cross-section of a rectangular bar or a normal rectangular element of a bar of any section.

Fig. 1.



When AB and CD are perpendicular to the plane of bending and AC and BD are parallel to this plane, it can be shown[†] that when the bar is uniformly bent AB and CD become concentric circular arcs each having a radius R_1 where

$$\frac{R}{R_1}=\sigma,$$

$$\sigma=\frac{\text{lateral contraction}}{\text{linear elongation}},$$

R = Radius of curvature of the mean line of the beam when strained.

For convenience we may term R the longitudinal radius and R_1 the transverse radius.

Thomson and Tait refer to rubber as a substance for which the curvatures may be easily observed. The earliest experimental demonstration for *metal* bars of the distortion of cross-section referred to above appears to be due to Franz Neumann. He attached mirrors to the vertical sides AC and BD of the rectangular section (fig. 1) and showed that the rectangle became a trapezium under the influence of a bending couple. He does not appear to have made a measurement of the ratio by this method; and I shall show later that although it is quite possible to demonstrate the distortion in this manner, it is not possible to obtain consistent values of the ratio $\frac{R}{R_1}$.

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[*] Communicated by the Author.

[†] Thomson and Tait's Nat. Philosophy, vol. ii. p. 260.

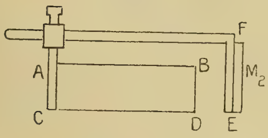
Searle, in his book on Experimental Elasticity, describes a method of measuring $\frac{R}{R_1}$ based on the principle we are considering. He attaches metal pointers to the vertical sides AC and BD (fig. 1) of the cross-section of the bar and determines the transverse radius R_1 from the motion of one pointer over a scale carried by the other. The mean value of σ which he obtained for a steel specimen was ·285, but the extreme observations from which this value was calculated differed from the mean by as much as 5 per cent.

I shall now describe some experiments which I carried out in order to determine this ratio for a steel bar of rectangular section.

First Method.

In my first experiments I attached one mirror, M_1, to the front face BD of the bar while the second mirror, M_2, was carried by a rod CAFE which was bent over, as shown in fig. 2, and soldered to AC. One mirror was fixed while the other could be rotated about horizontal and vertical axes and could also be displaced parallel to AB.

Fig. 2.

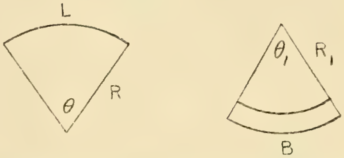


The two mirrors were adjusted as as to lie in the same plane, and two images of a scale placed about four feet away could be obtained side by side in the field of the telescope. The bar, the cross-section of which was 2·49 cm. × ·498 cm., was supported on two knife-edges placed 40·1 cm. apart. Two equal loads were applied at known equal distances beyond the knife-edges so that the bar became convex upwards.

In order to measure the *longitudinal curvature* a mirror was mounted above one knife-edge, and the image of a scale placed at a distance of 70 to 90 centimetres from the mirror was observed by means of a telescope. The curvature measured in this way is, of course, one-half of the total curvature. These observations were checked by placing a second mirror over the other knife-edge. The close agreement in the observed results showed that the arrangement was quite symmetrical, and that one mirror was sufficient.

To obtain the *transverse curvature* the scale readings corresponding to the mirrors M_1 and M_2 were noted in the telescope. The observed displacement is due partly to the rotations of the lines AC and BD (fig. 2) and partly to the rise of both mirrors with increase of load. From the displacement due to the rotation, we can calculate the angles through which the lines AC and BD have turned in the following way :—

Fig. 3.



Let L = distance between the knife-edges,
B = breadth of the bar,
S = distance of the longitudinal scale from its mirror,
S_1 = distance of transverse scale from its mirror,
D = deflexion on the longitudinal scale,
D_1 = deflexion on the transverse scale.

Then
$$\theta = \frac{L}{R} = \frac{D}{S},$$
$$\theta_1 = \frac{B}{R_1} = \frac{D_1}{2S_1},$$
$$\therefore \quad \sigma = \frac{R}{R_1} = \frac{S}{2S_1} \cdot \frac{L}{B} \cdot \frac{D_1}{D},$$
$$= k \cdot \frac{D_1}{D}.$$

Although the transverse scale was placed at a distance of about four feet from the mirror, the deflexion per kilogram on this scale was only 2 mm. when the corresponding deflexion on the other scale, due to the longitudinal curvature, was about 20 mm. Using this method I obtained eight values of σ lying between ·265 and ·280, the mean value being ·273.

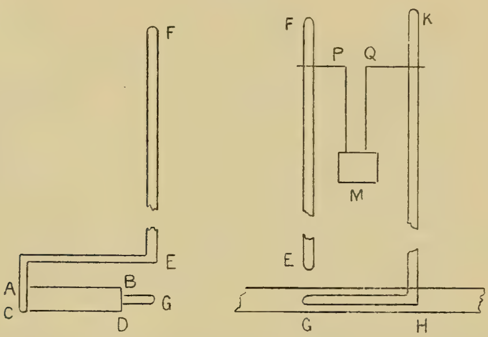
Since the deflexion corresponding to the transverse curvature is so small, a very small error in reading it produces a serious effect on the result. For a higher degree of accuracy to be attained it is clear that the transverse deflexion must be increased. In the second method which I employed this was secured, and the two deflexions were of the same order of magnitude.

Second Method.

In order to increase the transverse deflexion I made use of a device due to Lord Kelvin—the bifilar mirror.

A brass rod, CAEF, bent twice at right angles as shown in fig. 4, was soldered to the face AC at the middle point of the bar. The end G of a second rod, GHK, was soldered to the face BD, exactly opposite the point of attachment of the first rod. When a couple is applied to the bar the points K and F move in opposite directions, approximately at right angles to the plane of the paper, and the mirror M, which is suspended by silk fibres from the needles P and Q, rotates. A damping vane, immersed in oil, was attached to the mirror, and the latter was completely protected from draughts by means of a cardboard case fitted with a glass window.

Fig. 4.



Let θ_1 = the total angle turned through by AC and BD ;

a = mean heights of the needle points P and Q above the mean line of the bar ;

b = the mean distance between the fibres.

The mirror M turns through an angle θ_2 such that

$$\theta_2 = \frac{a}{b} \cdot \theta_1.$$

The formula used in the first method now becomes

$$\sigma = \frac{R}{R_1} = \frac{S}{2S_1} \cdot \frac{L}{B} \cdot \frac{b}{a} \cdot \frac{D_1}{D}.$$

As a was about 20 cm. and b about 1 cm., the deflexion on the transverse scale was 20 times as great as in the first method, and the longitudinal and transverse deflexions were of the same order of magnitude.

The lengths a and b were measured with a travelling microscope.

The results of experiments made by the second method are given in the following table.

Results.

Expt.	Load. kgrms.	Deflexion per kgrm.		Scale Distance.		a cm.	b cm.	Distance of Load from Knife-edge. cm.	$\sigma = \frac{R}{R_1}$.
		Long. Scale. mm.	Trans. Scale. mm.	Long. S. cm.	Trans. S_1. cm.				
1......	0–3	9·72	11·87	68·1	126·4	19·70	1·087	20·0	·2924
2......	...	12·10	14·82	...	...	...	...	25·0	·2932
3......	...	14·75	17·97	68·0	126·4	19·78	1·090	30·0	·2909
4......	...	14·75	18·10	...	...	...	...	30·0	·2930
5......	...	11·75	11·85	82·2	126·4	...	...	20·0	·2910
6......	...	11·70	11·85	...	...	...	...	20·0	·2923
7......	...	14·67	14·87	...	...	...	...	25·0	·2925
8......	...	14·67	14·87	...	...	...	...	25·0	·2925

$\mathrm{L} = 40·1$ cm. $\mathrm{B} = 2·49$ cm.

Mean Value of $\sigma = ·292$.

The bulk modulus k of an isotropic solid may be calculated from either of the two well-known equations

$$k = \frac{n\mathrm{E}}{3(3n - \mathrm{E})},$$

$$k = \frac{\mathrm{E}}{3(1 - 2\sigma)};$$

where E = Young's Modulus,
n = coefficient of rigidity,
σ = Poisson's Ratio.

An accurate knowledge of σ would enable us to calculate k from each of the above equations and determine from the degree of agreement in the results how far we were justified in using either of the equations to determine k.

Summary.

1. The object of the experiments was to determine Poisson's Ratio for a steel bar from observations on the distortion of the cross-section.

2. The first set of experiments indicated that the direct method of measuring the distortion, viz., by attaching mirrors to the two vertical sides of a bent bar, does not give consistent results.

3. The second set of experiments, in which a more sensitive indicating arrangement was used, gave eight values of σ, the lowest being ·2909 and the highest ·2932. The mean value was ·2922 and the maximum difference from the mean was ·44 per cent., that is rather less than $\frac{1}{2}$ per cent.

The experiments described above were carried out in the Physical Laboratory of the University of Bristol. I should like to take this opportunity of thanking Professor Selby of Cardiff for his valuable advice and criticism.

XCVI. *The Photo-electric Effect of some Compounds.*

By R. S. Willows, *M.A., D.Sc.*[*]

In the Phil. Mag. for September there is an interesting paper by Dr. A. Ll. Hughes with the above title. Among other results Dr. Hughes finds that dry zinc chloride shows no photo-electric effect, but when moist air is admitted to the apparatus relatively large currents are obtained, although water itself is not photo-electrically active. The purpose of the present note is to draw attention to some experiments by Mr. A. E. Garrett, carried out under my direction some years ago, which may throw light on the subject. Mr. Garrett and I had previously found that the halogen salts of zinc emit large quantities of positive and negative ions when they are heated to about 300°. In a second paper (Phil. Mag. June 1907) Mr. Garrett showed that the leak from these salts could be detected at the temperature of the room provided they were moist, but if moisture were excluded, little or no current was obtained even when the dry salt was heated to 360°. This, I believe, is the lowest temperature at which thermions have been detected. Dr. Hughes' electroscope is apparently more sensitive, and his method of obtaining the dry salt is certainly more efficient than Garrett's, so that any difference of electrical behaviour in the two states would readily be noticed. I am not clear from the paper whether the numbers given by Dr. Hughes represent the total leak, or the difference in the leaks when the salt is first obscured and then exposed to light. If the former, then the whole effect may be that measured by Garrett; while even in the latter case Garrett's experiments are not without interest, as they show that the salt is already in an instable condition and may easily be broken down by proper means, of which apparently ultra-violet radiation is one. It would be interesting to know whether a current was obtained with the accelerating field reversed, and, if so, how it compared with those given in the paper; in Garrett's experiments the positive ions were frequently in excess at low temperatures.

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[*] Communicated by the Author.

Cass Institute, E.C.

XCVII. *On Secondary γ rays excited by the β rays of Radium.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

Mr. CHADWICK, in his interesting paper on secondary γ-rays excited by the β-rays of radium (Phil. Mag. 1912, [6] xxiv. p. 594), deduces by analogy from the behaviour of the rays of radium that not more than 10 per cent. of the total γ-radiation of uranium X, observed by Mr. Russell and myself (ibid. 1909, xviii. p. 620), can be due to the impact of the β-rays on the platinum trays in which our preparations were contained. He seems not to have noticed that I had already shown by actual experiment with the rays themselves that the γ-rays of uranium X are not secondary rays produced by the impact of the β-rays (ibid. 1910, xix. p. 728).

In this paper, which Mr. Chadwick is evidently unaware of, he will find data as to the absorption of the γ-rays of uranium X in iron up to 0·92 cm. and lead up to 0·61 cm., together with the extrapolation of the absorption curves for greater thickness after they have become approximately exponential (fig. 1, plate xii.). He will, however, see from these curves that the values he assigns to his so-called absorption coefficients μ_1 and μ_2 have no meaning whatever apart from information, not provided, as to the material and the thickness of the material constituting the base of his ionization chamber A.

Frederick Soddy.

XCVIII. *On the Energy of the Groups of β rays from Radium.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN my paper entitled "The Origin of the β and γ Rays from Radioactive Substances" in the October number of this Journal, the energy E of the electron has been calculated from the formula $E=\frac{1}{2}m_0c^2\frac{\beta^2}{\sqrt{1-\beta^2}}$, where m_0 is the mass of the electron at slow speeds, c the velocity of light, and β the ratio of the velocity of the electron to the velocity of light. This is equivalent to multiplying the "transverse" mass of the electron by half the square of the velocity given by the Lorentz-Einstein formula. Mr. Moseley drew my attention to the fact, which I had overlooked, that according to the Lorentz-Einstein theory the total energy E of the electron is not given by the above formula but by $E=m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right)$. The latter formula agrees nearly with the former for small values of β, but departs widely from it when β approaches unity. Calculating on the latter formula the energy of the electrons comprising the different groups of homogeneous rays given in the paper of Danysz, the difference between the energies of successive groups can still be expressed by a relation of the same form as that given in the paper, viz. pE_1+qE_2, only E_1 and E_2 have new values. The values which fit in best with the data are $E_1=1{\cdot}12\times10^{13}e$ and $E_2={\cdot}356\times10^{13}e$; p has values between 0 and 9 and q between 0 and 2. All the twelve lines from Nos. 21 to 9 fit in with this relation except No. 11, which is nearly equal in energy to No. 10.

It may be significant that all the lines Nos. 8 to 1, which presumably belong to radium B, show an approximately constant difference of energy $E_3={\cdot}173\times10^{13}e$, which is very nearly one half of E_2. The observed and calculated energies from Nos. 8 to 1 agree within the probable limit of experimental error in the determination of the velocities. Line No. 9 fits in equally well with the radium B or radium C series, and it is not known to which series it belongs.

If the relation found by Whiddington (Proc. Roy. Soc. lxxxv. p. 323, 1911) between the velocity required to excite the characteristic radiations and the atomic weight depends on the energy of the electron rather than on its velocity, the energy of the electron to excite the characteristic radiation of the "K" series in radium C of atomic weight 214 is $1{\cdot}27\times10^{13}e$. Chapman (Proc. Roy. Soc. lxxxvi. p. 439, 1912) has shown that the characteristic radiation of the "L" series emitted by the heavier elements corresponds in penetrating power to the "K" type of radiation from an element of atomic weight $\frac{1}{2}(A-48)$. The corresponding energy to excite this characteristic radiation in radium C is $\cdot190\times10^{13}e$ ergs. It is of interest to note that these two values do not differ much from the values deduced for E_1 and E_3.

As I stated in my paper, the values of the velocities of the different groups of homogeneous rays from a product must be known with great accuracy before the correctness of such difference relations between the energies can be adequately tested. It is of great importance to know accurately the distribution of the β rays from active products both as regards velocity and number, for it is only with the help of such data that we can hope to explain the origin of the remarkable complex β radiation from active substances and its connexion with the γ rays.

E. Rutherford.

University of Manchester.
Nov. 4, 1912.

XCIX. *Notices respecting New Books.*

Gesammelte Werke Walther Ritz : Œuvres publiées par la Société Suisse de Physique. Paris : Gauthier-Villars, 1911.

WALTHER RITZ was born in 1878 at Sion in Valais, and died in 1909 at the age of thirty-one, after a brief but brilliant career as physicist and mathematician. In this book of collected papers, edited by Pierre Weiss, we have a fitting memorial of one whose early death robbed the world of a great investigator. His Inaugural Dissertation, *Zur Theorie der Serienspektren*, presented at Göttingen University in 1903, was immediately published in the *Annalen der Physik* and brought its author into the front rank. To find a reason for Balmer's law of frequencies in series of spectral lines was a problem to which Ritz returned again and again. He finally hit upon an electromagnetic mechanism in terms of which he was able to elucidate not only line-spectra, but also banded spectra and the Zeeman Effect. In his new method for solving differential equations in elasticity and potential he developed a valuable practical means of calculating to any required approximation the numerical values involved in any particular problem. Ritz also gave much attention to the general problem of electrodynamics and optics. In several papers he critically examined the necessity for the existence of the æther, and gave his verdict against it and in favour of atomic hypotheses. His aim was to construct a new theory in terms of attractions and repulsions of electrons; but, unfortunately, he was never able to present this theory in a distinct form. In this memorial of a short life we have ample evidence that Ritz was a man of rare mental gifts. His finished papers are powerful; his speculations have the touch of genius.

C. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 811.]

January 24th, 1912.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'The Upper Keuper (or Arden) Sandstone Group and Associated Rocks of Warwickshire.' By Charles Alfred Matley, D.Sc., F.G.S.

Under the name of the Arden Sandstone Group the author describes the stratigraphy of a sandstone zone in the Keuper Marls of Warwickshire, which is exceptionally well exposed in the area formerly occupied by the Forest of Arden.

This zone varies in lithological composition and thickness. It is never wholly a sandstone, but always contains beds of light-grey and pale-green shale, marl, and mudstone, which in places make up almost the whole of the zone. The sandstone, where present, usually forms thin, flaggy, white or light-grey beds, and exhibits ripple-marks, current-bedding, and surfaces with footprints and sun-cracks. The zone contains *Estheria minuta*; plants; teeth, spines, and scales of fishes; tracks and remains of labyrinthodonts and reptiles; and occasional casts of molluscan shells. The band is typically 20 to 25 feet thick, increasing sometimes to 40 feet or more; but it thins, especially eastwards and south-eastwards, to 4 or 5 feet.

The zone was first described by Murchison & Strickland in 1837, but has not hitherto been completely mapped. The author traces it from the type-locality at Shrewley over an area of 108 square miles, and finds that it forms a continuous deposit at an horizon between 120 and 160 feet below the base of the Rhætic. He accepts the view of Murchison & Strickland, that it is the same formation as the Upper Keuper Sandstone of Worcestershire and Gloucestershire, and he also correlates with it the similar deposit at Leicester described by Plant. The formation thus appears to have been laid down over an area at least 70 miles in length, and was probably formed, as an episode in the history of the Keuper Marls, by an irruption of the sea into the Keuper-Marl area. It represents a phase corresponding to that of the Rhætic Bone-Bed and the Tea-green Marls, but of somewhat earlier date.

The associated Keuper Marls have been examined, merely in order to establish their stratigraphical relations with the Arden Sandstone. So far as his observations go, the author is inclined to the view of the older observers that the Marls are aqueous deposits, though possibly containing much wind-borne material, deposited in a shallow lake undergoing strong evaporation and subjected to occasional irruptions of the sea. They represent the closing phase of Triassic 'continental' conditions in the English Midlands, when the slow subsidence which was soon to bring in marine Rhætic and Liassic deposits was in progress, and produced that overlapping of the Keuper rocks on to the higher grounds of the Triassic land-surface which is observable in the neighbouring districts of the Lickey Hills, Nuneaton, and Charnwood Forest.

The tectonics of the area are explained by sections and by a contour-map of the upper surface of the Arden Sandstone, which show that, while the beds as a whole are tilted south-eastwards, there are numerous shallow cross-folds with Charnian (north-west to south-east) axes and others with Pennine (north to south) axes. The majority of the faults have a Charnian trend.

The paper also records three well-borings through the Marls into the Lower Keuper Sandstone.

February 7th, 1912.—Prof. W. W. Watts, Sc.D., LL.D., M.Sc., F.R.S., President, in the Chair.

The following communication was read :—

'On an Inlier of Longmyndian and Cambrian at Pedwardine (Herefordshire).' By Arthur Hubert Cox, M.Sc., Ph.D., F.G.S.

The inlier in question comprises a strip of country about a mile in length and half a mile in breadth, situated near the border of Herefordshire and Radnorshire, about 15 miles south of Church Stretton. It lies on the well-known north-east and south-west line of dislocation which extends through that town.

Wenlock and Ludlow beds occupy most of the area around Pedwardine, but the occurrence of Cambrian Shale yielding *Dictyonema* has long been known. The *Dictyonema* Shales dip steeply westwards towards a series of red and green conglomerates and grits, with which an occasional thin shale-band is interbedded.

The latter beds, previously mapped as Llandovery, are here referred to the Longmyndian. They also dip steeply westwards, and have suffered considerable disturbance, accompanied by overthrusting from the west. They are quite unfossiliferous, and neither on lithological nor on structural grounds can they be regarded as Llandovery strata resting unconformably upon the Cambrian. Their nearest equivalents are found among the Longmyndian grits at Hopesay, and in the Bayston Group of the main Longmynd area. These Longmyndian grits at Pedwardine have apparently been carried south-eastwards over the Cambrian along an almost horizontal thrust-plane.

There is also present a small remnant of Bala grits which dip gently eastwards, and rest with strong unconformity upon the Cambrian shales. The undisturbed character of these Bala beds suggests that the neighbouring thrust may be of pre-Bala date.

Later faulting along a north-and-south line has brought the members of these older formations against Wenlock and Ludlow beds. From the greatly disturbed character of all the Silurian strata to the west of the inlier, as contrasted with the undisturbed condition of the beds on its eastern side, it would appear that this inlier is part of a barrier which has preserved the district lying to the east from the effects of the post-Silurian movements.

February 28th, 1912.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

The following communications were read:—

1. 'Late Glacial and post-Glacial Changes in the Lower Dee Valley.' By Leonard Johnston Wills, M.A., F.G.S., Fellow of King's College, Cambridge.

After pointing out that the district where the River Dee leaves its deep valley in the Welsh hills, and enters the lower ground occupied by the Coal Measures, is a critical one in connexion with its post-Glacial history, the author briefly describes the composition and local distribution of the Irish Sea and Welsh Drifts.

The second part of the paper deals with post-Glacial changes in the topography of the Dee Valley. The term 'post-Glacial' is here applied to events that occurred after the period of maximum glaciation. Many of the changes dealt with may have originated in late Glacial times.

In the Llangollen district the modifications are dependent on the serpentine course of the whole valley. Glacial phenomena have led to the cutting of overflow channels across the necks of the loops, at great heights above the river. Two of these have become permanent courses of the Dee, with the result that deep gorges have been formed across the rocks while the deserted loops have been left like gigantic oxbows.

The other diversions appear to be due to the fact that the post-Glacial course of the river was determined by the surface configuration of the Drift, and has since been excavated into the solid rock at places where it never flowed before. They are in fact cases of superimposed drainage.

An unimportant diversion at Argoed (near Trevor) is described, in which the river takes a longer course than in pre-Glacial times. The most notable change, however, occurs near Cefn, and involves the cutting of an entirely new course, some 10 miles long, between that locality and Eyton near Overton. Details of this gorge are given, and a suggestion is put forward to explain why the river took this course.

The general direction of this, the present, Dee valley is easterly. The pre-Glacial course has been traced southwards with some precision from near Cefn to Chirk, and then with less certainty in a more south-easterly direction for a few miles. In that direction the Drift is so thick, that it has been found impossible to trace the former course until it rejoins the deep buried valley which Dr. Strahan discovered in the neighbourhood of Chester. The author's observations have proved the continuation of this buried valley southwards nearly to Bangor-on-Dee. Near here, at Roden's Hall, the rock-surface is 30 feet below sea-level.

The southerly bend of the pre-Glacial valley near Cefn to Chirk, and then towards Whittington, suggests the possibility of a confluence of the Severn and the Dee, and this is shortly discussed.

It is shown that formerly the River Ceiriog joined the pre-Glacial Dee at Chirk, and that its present course below Chirk is post-Glacial. The gravels of this valley suggest that the post-Glacial drainage always followed this course. It is shown, however, that the Morlas Brook, which is now a tributary of the Ceiriog, was not always so, its early post-Glacial course having been to the Severn.

The slope of the pre-Glacial valley-floor and the uplift which is indicated by the buried valley, now many feet below sea-level, are briefly discussed.

2. 'The Glen Orchy Anticline (Argyllshire).' By Edward Battersby Bailey, B.A., F.G.S., and Murray Macgregor, M.A., B.Sc.

The district described stretches from the head of Loch Awe to Beinn Achallader, and is the south-eastern continuation of the Fort William, Ballachulish, and Appin country dealt with by one of the authors two years ago. The subject is the tectonics of the schists.

In the centre of the district a diagrammatic recumbent fold, of at least 2 miles in magnitude, is exposed to view in Beinn Udlaidh, in the heart of a gentle anticline, to which the name of the Glen Orchy Anticline is fittingly assigned. Around the western, southern, and eastern rim of this anticline, are found rocks which lie upon a structurally higher level than the Beinn Udlaidh Fold. A limestone, which occurs among these rocks, is correlated with the Ballachulish Limestone, and is believed to mark the core of the great, recumbent, Ballachulish Fold, everywhere, in this district, underlain by the Ballachulish Slide (fold-fault). Incidentally, this interpretation involves a displacement of at least 24 miles along the Ballachulish Slide. Finally, an important inversion of the Ballachulish Limestone and Slide is discussed in connexion with a description of the Beinn Doirean and Beinn Achallader range of mountains on the east side of the Glen Orchy Anticline.

March 13th, 1912.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

The following communications were read:—

1. 'On the Glacial Origin of the Clay-with-Flints of Buckinghamshire, and on a Former Course of the Thames.' By Robert Lionel Sherlock, D.Sc., A.R.C.S., F.G.S., and Arthur Henry Noble, B.A., F.G.S.

The paper is founded on observations made during the mapping of some 260 square miles on the 6-inch scale, in Buckinghamshire, Berkshire, Hertfordshire, and Middlesex.

The superficial deposits are divided into Clay-with-Flints with the associated Gravelly Drift, and the Fluvioglacial Gravels. There are, in addition, certain high-level gravels, older than any of these, and also the river-gravels and alluvium of the present streams, none of which deposits are dealt with in the paper.

Evidence is given to show that the Clay-with-Flints and Gravelly Drift were formed by an ice-sheet which came from the north or north-west over the Chiltern Hills. Only the clean upper layers of ice surmounted the escarpment, and this produced the Clay-with-Flints and Gravelly Drift from the 'head' (Chalk and Eocene waste), which had been accumulating for ages.

At that time the Thames flowed, at the foot of the Eocene escarpment, from Bourne End through Beaconsfield and Rickmansworth to Watford. The ice-sheet blocked the river-channel between Bourne End and Rickmansworth about the time of maximum cold and diverted the Thames southwards at Bourne End. The river beyond Watford was further blocked by the Eastern Drift, which has left Boulder Clay near Hatfield and at Finchley. The section of the river between Rickmansworth and the Eastern Drift had its direction of drainage reversed, and the water escaped at Rickmansworth by a new channel which became the Colne.

On the melting of the ice, Fluvioglacial Gravels (Plateau Gravels of some writers) were left over a great area. These gravels are composed chiefly of Eocene and Cretaceous materials derived from the Gravelly Drift, but also contain Bunter pebbles which have been brought down the Thames. The Bunter pebbles are particularly abundant in a band between Bourne End and Watford; to the south only a few, presumably washed out of the band, are found. They are believed to show that the Thames in times of flood returned to its former course.

The floods from the melting ice, added to the waters of the Thames and Colne, produced, by denudation of the Eocene clays, the great flat through which the Thames now flows, east of Maidenhead, and which, opposite Iver, is 8 miles wide.

After the retreat of the ice, the Wye and Misbourne extended their channels over the Fluvioglacial Gravel flat, and some other small streams were formed.

2. 'Some New Lower Carboniferous Gasteropoda.' By Mrs. Jane Longstaff (*née* Donald), F.L.S.

March 27th, 1912.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Glaciation of the Black Combe District (Cumberland).' By Bernard Smith, M.A., F.G.S.

After a brief discussion of previous work and literature, a short sketch is given of the geological structure of the district.

With the exception of the western coastal plain the main topographical features are pre-Glacial, but they have been either subdued or accentuated by glaciation. The chief pre-Glacial drainage-lines determined those of the present day.

Evidence is given to show that, during the flood-tide of glacial tion, the whole district was swamped beneath an ice-sheet formed by the confluence of Lake District and Irish Sea ice, the summit of Black Combe (1969 feet) being over-ridden by ice which was comparatively clean.

The Lake District ice travelled from the Broughton Valley, the Duddon Valley and high ground to the west, and from Eskdale. Near the coast-line the overmastering pressure of the Irish Sea glacier diverted the seaward flow of the Lake District ice to the south or south-east.

The deposits of the Lake District ice are briefly described, and a more detailed description is given of the deposits of the Irish-Sea ice which are exposed in the sea-cliffs of the coastal plain. The distribution of Scottish boulders is also discussed.

In the Lower Boulder Clay of the westward mountain-slopes (the ground-moraine of combined Lake District and Irish Sea ice) there is evidence both of the interweaving of drifts of distant and strictly local origin, and of a certain amount of movement of ice inland.

Phenomena which occurred during the withdrawal of the ice are next described under the following heads:—

(1) Moraines and trails of boulders.

(2) Marginal channels and associated sands and gravels.—The trend of these channels is, in the best examples, parallel to the coast and nearly at right angles to the present drainage-lines. In some cases the channels were carriers of the ordinary marginal drainage of the ice-sheet, in other cases they were cut by overflow waters from impounded lakelets. Before the cutting of the channels between Eskdale and Bootle the ice overrode a series of sands and gravels formed, chiefly as a marginal outwash-fan, at a slightly earlier date.

(3) Sand and gravel of the plain.—These deposits are considered to have been accumulated after the formation of the channels near Bootle, the material being in the main deposited in embayments of the margin of the Irish Sea ice.

(4) The Whicham Valley and Duddon Estuary Lakes.—Sand and gravel was also accumulated at the extremities of ice-lobes which were thrust into the mouths of valleys, so that the normal drainage of these valleys was obstructed. The ice-dammed Whicham Valley Lake is described in detail: it drained at first into the Duddon Estuary by the Gill Scar channel, but afterwards through the obstructing barrier—reversing the flow of water.

The Upper Boulder Clay is then briefly discussed, and some account is given of late corrie-glaciation.

In conclusion, certain hanging valleys are shown to be due to the oversteepening of hill-slopes, or overdeepening of main valleys during the maximum glaciation.

2. 'The Older Palæozoic Succession of the Duddon Estuary.' By John Frederick Norman Green, B.A., F.G.S.

The Lower Palæozoic geology of the estuary of the Duddon, which separates Cumberland and Lancashire, has been little studied, but is of especial interest, because the (?) Skiddaw Slate, Volcanic Series, and Coniston Limestone Series are in proximity along an outcrop of several miles, and the alteration is generally less than in other parts of the Lake District. The following succession is described in descending order :—

	Thickness in feet.	
Limestones (Sleddale Group)	100	
Stile End Beds	40	
(unconformity)		
Upper Tuffs	40	Volcanic group, 650 feet.
Rhyolites	60	
Harrath Tuffs	100	
Middle Tuffs	300	
Dog Crag Tuffs	50	
Mottled shale	100	
Blue shale or (?) Skiddaw Slate—no base seen.		

The blue shale and mottled shale are described; and it is shown that the latter is identical with the former, except for the addition of lapilli of andesite-glass and slate. Tuff-free bands, indistinguishable from blue shale, are intercalated. Conformity is also proved by mapping and by sections exposing the junction.

The Dog Crag type is of the same material as the mottled shale, but with little muddy matrix, and passes up into the bedded Middle Tuffs, composed of fine-grained débris; these in turn pass up into the Harrath type, marked by fragments of variolite and, in the upper part, felsite. The rhyolites are considered to be substantially contemporaneous. The thin andesitic Upper Tuffs are only seen in the neighbourhood of Millom.

The pyroxene-andesites of the district are briefly described. They vary from acid forms with oligoclase in the ground-mass and felspar-phenocrysts, to forms with an andesine-augite matrix and augite-phenocrysts. They occur sporadically in any horizon from the Skiddaw Slate to the rhyolites, and in many cases are certainly intrusive. The sills metamorphose the Middle Tuffs near their margins into 'hälleflintas.'

It is next shown that the whole succession has been thrown into folds with axes trending north-east and south-west, and now lies in folded sheets with a low dip, though the bedding-dips are high. This folding having been determined, it is possible to decide the relationship of the Coniston Limestone Series to the underlying beds. Near Millom the Upper Tuffs and Stile End Beds are developed. The latter are composed of detrital igneous matter. At Waterblean the Stile End Beds disappear. At Graystone House, near Duddon Bridge, where an important exposure of fossiliferous limestone was discovered among the volcanic rocks by Sedgwick, the Upper Tuffs are also absent. On the east side of the estuary, mapping shows the limestone lying upon the Dog Crag type, the mottled shale, and the blue shale or andesite. The conclusion that an unconformity exists was confirmed by a trench cutting Coniston Limestone resting upon undisturbed intrusive augite-andesite.

The existence of a powerful strike-fault is proved by the position of the Graystone House Limestone and by repetition of the upper part of the volcanic group.

CI. *Intelligence and Miscellaneous Articles.*

THE DIFFUSION OF ALKALI SALT VAPOURS IN FLAMES.

The Rice Institute,
Houston,
Texas, U.S.A.
Oct. 25, 1912.

To the Editors of the Philosophical Magazine.

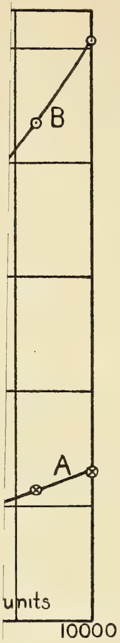
Gentlemen,—

IN reply to Mr. A. Becker's letter published in the Philosophical Magazine for October 1912, I beg to say that I very much regret that I was not acquainted with his previous work on the diffusion of alkali salt vapours in flames when I wrote my paper on that subject which appeared in your July number. Unfortunately the publications of the Heidelberg Academy of Sciences are not accessible to me. As to my measurement of the velocity of the flame gases, it was not my intention to claim any novelty. Similar methods had previously been used by various people, and as I only required a rough estimate of the velocity I considered the rough method I adopted sufficient for the purpose. I did not suppose anyone would desire to be known as the inventor of the method I used.

I do not consider methods depending on the force exerted on a small ball by the stream of gas as likely to be exact, since they must require a knowledge of the coefficient of viscosity of the flame gases, a quantity which can scarcely be found with any exactness. I think that the very considerable divergence between the values found for such quantities as ionic velocities and coefficients of diffusion in flames by different observers is partly due to differences between the flames used. These quantities undoubtedly vary very much in different parts of the same flame, and large differences must occur in different flames. I think it quite possible that Mr. Becker's flames have been colder than mine to an extent sufficient to account for the smaller value he obtained for the coefficient of diffusion of sodium vapour. In my experiments I also used lithium, potassium, rubidium, and cæsium vapours, and obtained consistent results with all these metals. The possible errors in such experiments are certainly very large, and I have no desire to claim greater accuracy for my work than for that of others.

Yours very truly,

Harold A. Wilson.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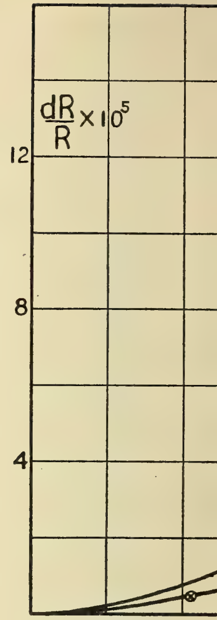
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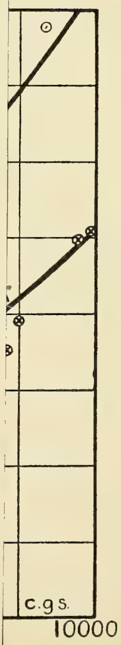
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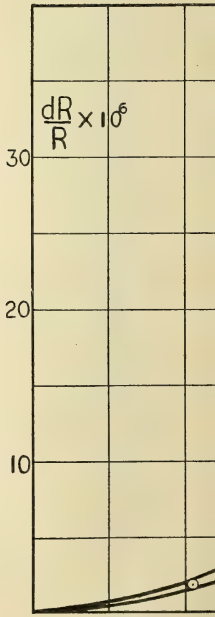
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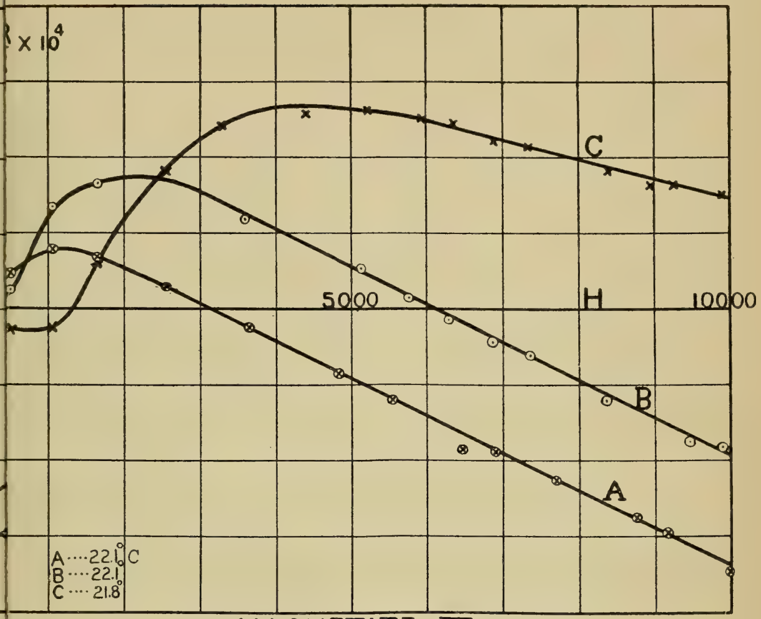
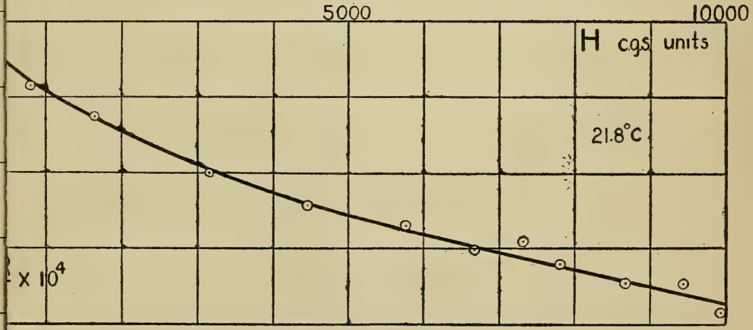
Fig. 7.



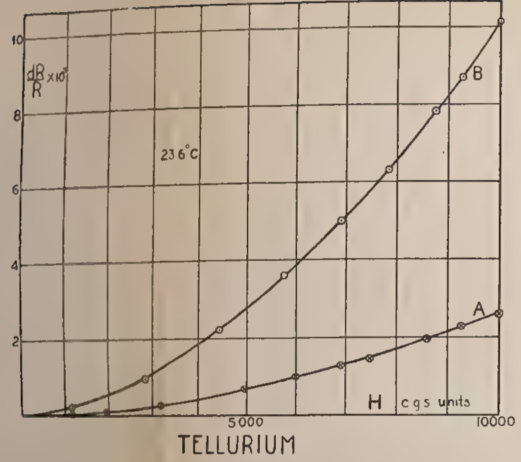
MAGNETITE III.

Fig. 8.



MOLYBDENITE

Fig. 1.



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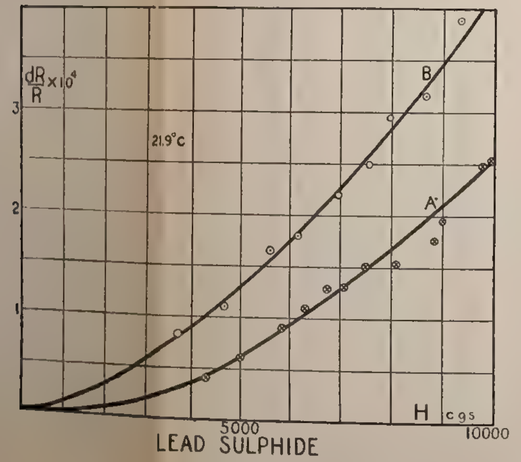


Fig. 3.

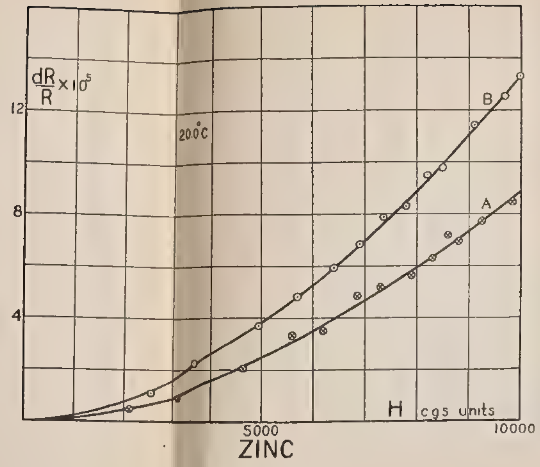


Fig. 4.

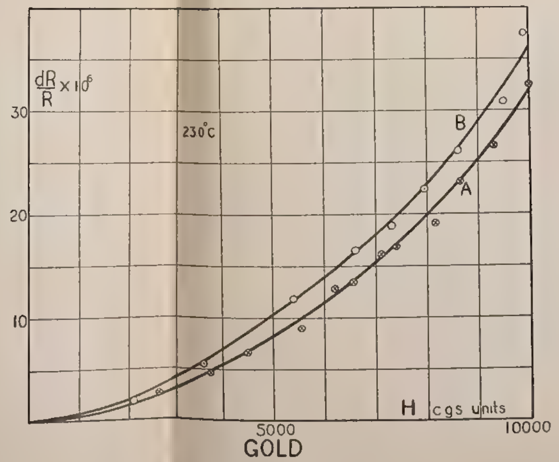


Fig. 5.

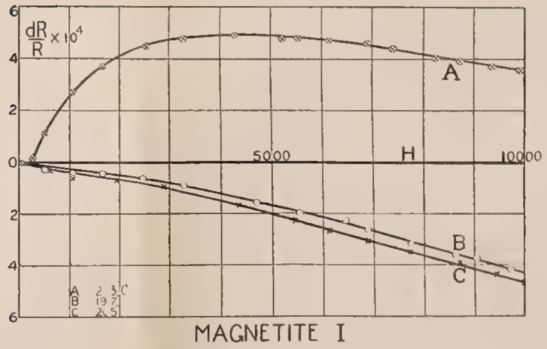


Fig. 6.

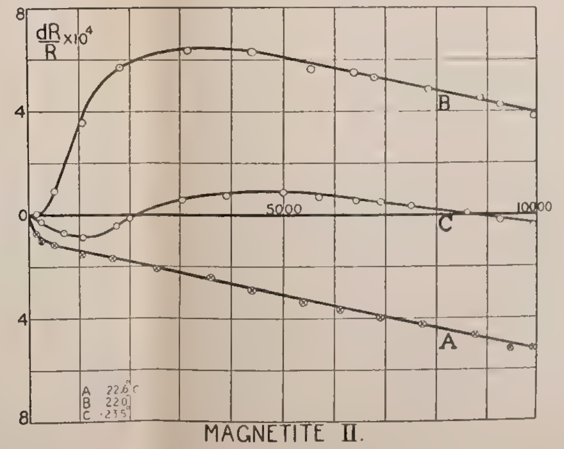


Fig. 7.

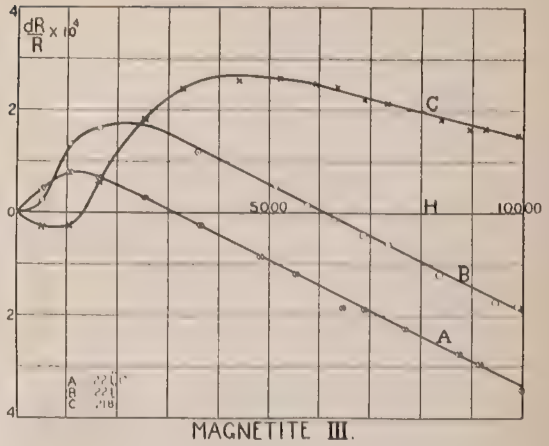
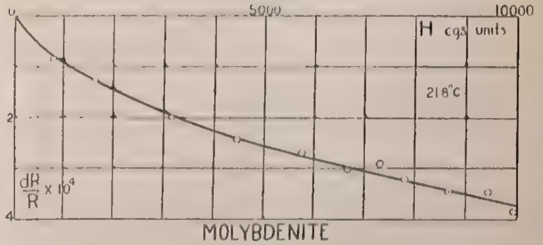


Fig. 8.



B

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